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ON THE SPEED OF REDUCTION OF FERRIC ALUM BY SUGAR.

BY J. H. LONG.

Received July 7, 1897.

IN two papers published last year in this Journal, I gave numerous experiments on the inversion of cane sugar solutions by various salts. In several cases certain secondary reactions were noticed, but they were not discussed at length, as they had no direct bearing on the problem in hand. Certain salts were found to invert sugar and to become reduced or otherwise changed at the same time. A good illustration of this is a mixture of ferric alum and sugar, in which inversion of the sugar and reduction of the iron salt take place rapidly on warming, and even on standing in bright sunlight through several warm days. A somewhat analogous change takes place with solutions containing chrome alum, but this was not followed in detail.

On June 4, 1896, a solution was prepared containing in 250 cc., fifty grams of pure cane sugar and ten grams of ferric alum; this had the usual dark color. It was allowed to stand in the light two weeks. At the end of the first week the color had changed to light green, with apparent conversion of the ferric to ferrous salt. On June 18, a polarization was made, giving $\alpha = -3.85°$ in a 100 mm. tube, at 20°. A test made some days later showed the same results. This doubtless corresponds to complete reduction, as the theoretical end reading of $-4.3°$ is not reached in such a mixture, as I pointed out in my papers referred to, and possibly from an alteration of a little of the levu-

lose. The solution was found also to contain free sulphuric acid, and an approximate titration showed this to correspond in amount to what should be expected from a conversion of ferric into ferrous sulphate. It is not possible here to measure the rate of inversion, because of the dark color of the liquid, until near the end, and this was not attempted.

At first sight it appeared possible to measure the rate of reduction of the ferric salt from the change of color during the reaction, but this was not found satisfactory, even by the aid of an excellent spectro-photometer, and the conversion of the ferric salt into thiocyanate. Two reasons may be given for this; it is well known that the color of a ferric solution varies greatly with the temperature, and this alone makes an accurate observation difficult with the ordinary instruments; further, it has been shown by Krüss that no accurate relation exists, in the case of ferric thiocyanate, between concentration and extinction coefficient. My own experiment confirms this view.

As may be easily seen, the usual methods of determining ferric in the presence of ferrous salts can not be applied here, because of the presence of the great excess of organic matter, and I therefore gave up all attempts to make direct determinations. On consideration of the reaction which must take place in the reduction, however, a possible method soon presented itself, and this on trial was found to be very satisfactory. Considering the iron salt alone in the alum, the reaction is this:

$$Fe_2(SO_4)_3 + H_2O = 2FeSO_4 + H_2SO_4 + O.$$

Ferrous sulphate and free sulphuric acid are formed and remain in solution, while oxygen is liberated and is absorbed in the oxidation of a part of the sugar.

The text-books are practically silent on the subject of the oxidation of sugar by heavy salts in neutral or acid solution. Even less seems to be known concerning the products of such oxidation than is known for the Fehling and similar reactions in the presence of alkali. In an experiment on the subject, the following observations were made: I dissolved fifty grams of pure cane sugar in water and mixed with it fifty grams of ferric alum in solution; the mixture was diluted to 250 cc. and heated in a flask with a capillary stopper to 85° C. In about an hour the color of the liquid had become greenish, indicating reduc-

tion to the ferrous condition, but on longer heating the solution grew darker and became finally dark brown. During the last stage of the heating numerous gas bubbles escaped from the liquid, suggesting active decomposition. With lime water these bubbles gave a precipitate. In a second similar experiment the apparatus was arranged to permit the collection of this gas. For this purpose a sulphuric acid bulb was attached to the delivery tube from the flask, and beyond this a weighed potash bulb. After the evolution of the gas had ceased the increase of weight in the potash bulb was found to be 0.015 gram. Although this amount is not large, it is sufficient to indicate that a small portion of the sugar undergoes advanced oxidation. What the principal changes are lies outside the scope of this investigation.

If, as suggested above, a direct reduction of the ferric salt is effected, the change is one which should be easily followed by a series of electrical conductivity determinations, and this hypothesis I was soon able to confirm by simple experiments. With decomposition of the complex ferric salt into the simpler ferrous salt and free acid a marked increase in conductivity should be noticed, and that this is the case, the following experiment shows. I made up a thick syrup with ferric alum and determined its resistance in a U cell of the Kohlrausch type at 20.2°, and found it to be 406 ohms. After standing several days in January, in diffused light, I found at 20° 407.5 ohms; that is, practically, no change. I next heated the solution through five hours to a temperature of 70° in a flask closed with a rubber stopper and long capillary tube. After cooling a new test was made, showing now a resistance of 197.2 ohms at 20°.

Another solution was made containing in 500 cc. fifty grams of sugar and 48.2 grams of pure ferric alum. The resistance of this was found to be 396.6 ohms at 20.3° in the same apparatus. A portion of this solution was allowed to stand four months exposed to the light, when a new test was made. It was then green in color, but still contained a little ferric salt. The resistance at 20° was found to be 199.5 ohms. Part of the same solution stood through the same period in a dark cupboard and at a higher mean temperature. It remained yellowish brown, and gave in the same apparatus a resistance of 323.3 ohms at 20°.

The influence of the light is very clearly indicated by the above tests.

As is well known, dilute solutions of ferric alum are not stable, even at the ordinary temperature, while relatively strong solutions decompose when heated. To follow the rate of reduction accurately, it is desirable to choose such a concentration and such a temperature that the whole change may be completed in a single working day, that is, within eight or ten hours. A mixture containing 15.0625 grams of ferric alum and 100 grams of sugar in 500 cc. was tried, but as it became turbid at 70°, after a time, was discarded. The same was found true of the solution, referred to above, containing in 500 cc. 48.2 grams of alum and fifty grams of sugar. It was found practically that the most stable solutions were those made with large amounts of ferric salt, the weight of sugar present being of far less importance. After a few trials the following solution was found to have the required stability and to satisfy all demands: Ferric alum, 120.05 grams; sugar, 100 grams; water to make 500 cc. This is a fourth normal solution, as it contains one molecule of alum in four liters. Many of the following experiments were made with a solution of this concentration. It was found to have a resistance of 282 ohms at 20° in the cell used throughout all the tests; this corresponds to a molecular conductivity, $10^3\mu = 111.4$, the factor for reduction being determined by fiftieth-normal potassium chloride and saturated sodium chloride solutions. The following table shows the variation in the value of μ with dilution:

TABLE I.

V, liters.	$10\mu^3$.
4	111.4
8	179.5
16	248.5
32	318.0
64	388.1
128	467.5
256	567.0
512	692.3
1024	846.4
2048	1093.5

The solutions became somewhat turbid before the end of the experiments, which were conducted as rapidly as possible. The

last values show that dissociation was far from complete. When a portion of the undiluted solution was heated to 75° through five hours, it became yellowish green and completely reduced. The resistance for this was found to be 126.6 ohms, corresponding to $\mu = 248.1 \times 10^{-3}$, for the original ferric salt. On diluting the product the conductivities were found as shown in the table below, the dilution being referred to the ferric salt originally present.

TABLE II.

V, liters.	$10^3\mu$.
4	248.1
8	390.4
16	506.6
32	612.8
64	716.7
128	823.8
256	930.6
512	1037.5
1024	1141.2
2048	1244.0

The solutions remained perfectly clear throughout, and ionization appears to be more nearly complete than before. By repeating these experiments several times with fresh prepaiations of ferric alum, slightly different values were found for the original resistances and those after reduction. The limits for the first were 281.5 to 282.5, and for the last 125 to 127.

In the reduction of the ferric alum, ferrous sulphate, ammonium sulphate and free sulphuric acid are formed. I next prepared a solution of these substances in the proportions which would result from the reduction of the amount of ferric alum taken above. The solution contained:

	Grams.
Sugar	100.0
Crystallized ferrous sulphate	69.5
Ammonium sulphate	16.5
	cc.
Normal sulphuric acid	250
Water to make	500

With this solution a resistance of 125.8 ohms was found at 20.5°, which corresponds very closely to 127 ohms at 20°. Indeed, this result is much closer than one at first thought

might expect, when it is remembered that a part of the sugar suffers oxidation during the reduction of the salt. But practically the same figures were found in many subsequent trials, from which it is evident that the resistance of the sugar is not greatly changed by inversion and partial oxidation. It is probable that the products formed are but slightly dissociated. A few experiments were made to throw light on this point. A solution was prepared containing in 250 cc. 60.25 grams of ferric alum and an amount of pure dry crystallized dextrose to correspond to fifty grams of cane sugar (52.6 grams). The resistance of this at 20.5°, was found to be 279.2 ohms. The resistance of dextrose is therefore practically the same as that of cane sugar. This solution was heated to 70° through several hours, but still remained yellowish brown, and deposited finally a basic precipitate. A solution was next made containing in 250 cc. fifty grams of dextrose, fifty-five grams of ferric alum and twenty-five cc. of normal sulphuric acid. The resistance was found to be 230.5 ohms at 20.2°. A portion of the solution was heated two hours at 95°; it remained dark and deposited a slight basic precipitate. The resistance was now found to be 195.6 ohms at 20.3°, which is a relatively small change. Finally I made a solution with fifty grams of cane sugar, 60.25 grams of ferric alum and twenty-five cc. of normal sulphuric acid in 250 cc. The sugar was inverted by the acid before the alum was added, and for the mixture a resistance of 244.3 ohms at 20.2° was found. After heating to 95° through two hours, the resistance was reduced to 111 ohms at 20°, while tests showed the ferric salt to be wholly reduced. It would appear from the above that the reduction is largely due to the levulose of the inverted sugar, and this agrees with the known behavior of levulose in other reactions.

That the resistance after reduction corresponds closely to that found from mixtures of the reduction products according to the equations assumed above, was found in other cases where larger and smaller amounts of sugar were used with the given weights of the salts. This established, we have evidently a very simple means at hand for determining the speed of the reduction reaction, by determination of resistances from time to time, the results being compared with the resistances found from known mixtures

of acid, ferric and ferrous salts and ammonium sulphate. These mixtures were made to contain amounts of ferric alum, ferrous sulphate, ammonium sulphate and acid corresponding to those present at different stages in the reduction. In the following table are given the weights of the pure materials mixed, the iron salts being taken in the crystallized condition.

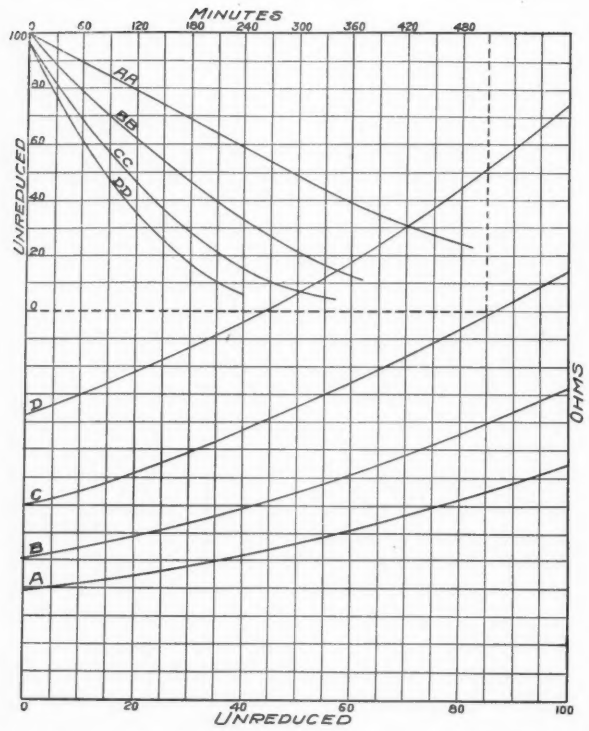
TABLE III.

For 250 cc. of Solution.

Sugar. Grams.	Ferric alum. Grams.	Ferrous sulphate. Grams.	Ammonium sulphate. Grams.	Normal sulphuric acid. cc.	Ferric salt. Per cent.	Resistance in ohms.
50	60.25	....	....	..	100	282.1
50	48.20	6.95	1.65	25	80	241.6
50	36.15	13.90	3.30	50	60	204.6
50	24.10	20.85	4.95	75	40	173.2
50	12.05	27.80	6.60	100	20	148.3
50	....	34.75	8.25	125	00	126.6

In the last column the resistances in ohms for the several solutions are given. I have not thought it necessary to calculate the corresponding conductivities, as the direct determinations are sufficient for all comparisons to be made. By means of coordinate paper, I have plotted a curve from these values on a large scale, and from this curve the resistance of any intermediate mixture may be found with a high degree of accuracy. The form of this curve is shown in the accompanying figure at *B*. In making the above mixtures the ferric alum was dissolved in part of the water by the aid of heat; the solution was then cooled to 20°. The sugar and the other substances were then dissolved in more water, the cooled mixture was added to the ferric alum and the whole brought to 250 cc. at 20°. At this temperature the ferric alum changes very slowly, and not appreciably during the time of an experiment. The sugar in the mixtures was probably mostly in the inverted condition. Experiments with mixtures, as in the above table, were repeated several times and always practically with the same results.

The data secured in the manner described were applied to follow the speed of reduction in a solution warmed in the thermostat. I made a solution with 241 grams of ferric alum in 500 cc. at 20°, and another with 200 grams of sugar in 500 cc. These solutions were warmed to 70° and mixed. The mixture



was divided among eight flasks holding over 100 cc. each. The flasks were closed with capillary stoppers and were supported in a frame to be immersed in the thermostat and rotated. While being filled, the flasks were kept at a temperature of 66°, and this was the exact temperature of the thermostat in all experiments. The liquids mixed at 70° cooled to about 66° during the filling, and after immersion in the water the flasks remained fifteen minutes before the first one was removed for an observation; this to allow the temperature to become constant. Some preliminary experiments were carried out at a temperature of 75°, but here it was found that the reaction was completed too quickly for accurate observation. In another series of tests at 55° the time required to complete the tests was found to be too

long. Finally 66° was chosen as the temperature best suited to all the experiments contemplated.

In the table below the results obtained by testing the solutions from the eight flasks are given. The first column shows the time at which each flask was removed from the thermostat and quickly cooled. The second column shows the resistance found at 20°, while in the third column the amount of ferric salt remaining is expressed in per cent. for each test.

TABLE IV.

Time.	Ohms.	Unreduced.
9.00	281.4	99.5
9.30	262.9	90.5
10.00	240.6	79.3
11.00	207.9	62.5
12.00	182.5	46.8
1.00	163.6	33.0
2.00	149.6	21.6
3.00	140.4	13.5

The numbers in the third column are obtained by interpolation from the curve referred to above. When these numbers are plotted in the same manner, with the times in minutes (duration of heating) as abscissas, a very regular curve, shown at *BB*, is obtained. An inspection of the curve and the table is sufficient to show that the speed of the reduction decreases slowly at the start; the law of the reduction is not immediately apparent, but this will be taken up later.

It was thought best to make other tests with larger and smaller amounts of sugar, and the results of these will be given below. As preliminary, however, I determined roughly the behavior of constant amounts of ferric alum with varying amounts of sugar, and this is shown in the following table. Five solutions of 100 cc. each were made, and these were heated three hours to 75° in the thermostat.

TABLE V.

No.	Amount of alum.	Amount of sugar.	Ratio of of alum to sugar. Mol.	Results.
1	24.1	4.275	1 : $\frac{1}{2}$	Heavy basic precipitate.
2	24.1	8.550	1 : 1	Slight precipitate.
3	24.1	17.10	1 : 2	Clear, slightly colored.
4	24.1	25.65	1 : 3	Clear, dark.
5	24.1	34.20	1 : 4	Clear, dark.

It is evident, therefore, that the proportion of sugar in the first is much too low; in the second it is slightly low, while in the others it is sufficient.

I made next solutions of 250 cc., with the amounts of sugar and salts as shown in the following table, and found the corresponding resistances given in the last column, in ohms at 20°.

TABLE VI.

For 250 cc. of Solution.

Sugar. Grams.	Ferric alum. Grams.	Ferrous sulphate. Grams.	Ammonium sulphate. Grams.	Normal sulphuric acid. cc.	Ferric salt. Per cent.	Resistance in ohms.
25	60.25	....	....	....	100	213.0
25	48.20	6.95	1.65	25	80	181.0
25	36.15	13.90	3.30	50	60	152.5
25	24.10	20.85	4.95	75	40	130.0
25	12.05	27.80	6.60	100	20	111.2
25	....	34.75	8.25	125	00	96.2

A curve plotted from these figures is shown at *A*. This curve was used as before to calculate the proportions of ferric and ferrous salts, in mixtures undergoing reduction, from observations of resistance.

A solution for the thermostat was prepared containing in 1000 cc. 100 grams of sugar and 241 grams of ferric alum. As in the former case, the sugar and alum were dissolved separately and made up to 500 cc., mixed and distributed in the small flasks as before. The table below gives the result of the tests, the thermostat being kept at 66°, and the first flask removed at the end of fifteen minutes.

TABLE VII.

Time.	Ohms.	Unreduced.
9.00	213.6	100.0
10.30	190.4	86.0
12.00	165.0	69.5
1.00	151.3	59.0
2.00	138.8	48.5
3.00	129.4	40.0
4.00	121.5	31.6
5.00	115.5	25.5

The results of the last column are plotted and shown at *AA*. It will be observed that the rate of reduction is much slower here than in the former case. It was also noticed that the last

flasks removed from the thermostat were slightly turbid from partial dissociation.

Two other sets of solutions were studied. The details of the results are here given.

TABLE VIII.

For 250 cc. of Solution.

Sugar. Grams.	Ferric alum. Grams.	Ferrous sulphate. Grams.	Ammonium sulphate. Grams.	Normal sulphuric acid. cc.	Ferric salt. Per cent.	Resistance in ohms.
75	60.25	....	...	...	100	386.5
75	48.20	6.95	1.65	25	80	333.5
75	36.15	13.90	3.30	50	60	285.0
75	24.10	20.85	4.95	75	40	243.2
75	12.05	27.80	6.60	100	20	206.4
75	....	34.75	8.25	125	00	177.1

In curve *C* the results of the observations are found plotted. A mixture of 300 grams of sugar and 241 grams of ferric alum was made and used in the thermostat as before. The resistance found and the amount of reduction are tabulated below.

TABLE IX.

Time.	Ohms.	Unreduced.
8.30	379.1	97.4
9.30	304.4	68.5
10.15	264.8	50.5
11.00	237.3	37.0
11.45	214.7	25.0
12.30	199.8	16.0
1.15	191.2	10.0
2.00	184.4	5.5

The results of this test are plotted and shown in curve *CC*, which is very regular, without any sharp breaks.

Finally a series of concentrated solutions were made to fully test the effect of increased amounts of sugar on the speed of the reaction. It was found that 400 grams to the liter could be brought into solution with the amount of salts taken, and the table below shows the results obtained with such mixtures.

TABLE X.

For 250 cc. of Solution.

Sugar. Grams.	Ferric alum. Grams.	Ferrous sulphate. Grams.	Ammonium sulphate. Grams.	Normal sulphuric acid. cc.	Ferric salt. Per cent.	Resistance in ohms.
100	60.25	....	..	...	100	538.0
100	48.20	6.95	1.65	25	80	462.3
100	36.15	13.90	3.30	50	60	397.5
100	24.10	20.85	4.95	75	40	341.2
100	12.05	27.80	6.60	100	20	296.0
100	....	34.75	8.25	125	00	261.0

Curve *D* was plotted from these observations.

A corresponding mixture with 400 grams of sugar and 241 grams of ferric alum was then investigated after heating in the thermostat to 66° as before. The results show a greater rapidity in the reduction of the ferric salt than was found in either of the other mixtures, as indicated in the following table.

TABLE XI.

Time.	Ohms.	Unreduced.
8.45	530.4	98.0
9.00	490.9	87.5
9.30	428.8	70.0
10.00	381.2	54.5
10.45	332.9	36.5
11.35	296.1	20.0
12.20	279.4	11.0
12.45	273.3	7.0

The curve *DD*, plotted from the figures of the last column is, like the last one, very regular.

The question now presents itself, What is the law governing the rate of reduction of ferric salt? In all cases the amount of sugar is relatively great in proportion to that of the salt, if we take as our basis of comparison the salt and sugar which react in the well known Fehling test. But it must be noted that the oxidation here is much less complete than it is in that case, extending probably, to a small portion of the levulose formed only. Because of the uncertainty as to the exact nature of the reaction between the two substances taken, it would appear at first view that the rate of reduction can not be accurately expressed by a formula, but as the sugar is certainly in excess in some cases, I have calculated the speed of the reduction on the assumption that the iron salt alone undergoes a change in the reaction. From what was shown in one of the experiments cited above, it appears probable that the invert sugar, and not the cane sugar, is the reducing agent, and, further, that from the very beginning of the reaction, enough of this is possibly present to absorb all the oxygen furnished. It is also true that most of the invert sugar is still present at the end of the reaction. Looking upon the change, therefore, as a reaction of the first order, we have

$$\frac{dx}{dt} = K(A - x),$$

where A represents the ferric salt present at the beginning of the experiment, and x that reduced at the time, t. Therefore as $x = 0$ for $t = 0$, we have:

$$K = \frac{1}{t} \text{ nat log } \frac{A}{A - x}.$$

The calculations below are made with common logarithms, as only the relative, not the actual values are considered. Table XII gives the value of K for the weakest of the above solutions, while in the three following tables the values for the other solutions are given.

TABLE XII.

100 Grams Solution. $A = 100$.

t.	x.	$\log \frac{A}{A-x}$.	$\frac{1}{t} \log \frac{A}{A-x}$.
0	0	.....	.....
90	14.0	0.06550	0.00073
180	30.5	0.15802	0.00088
240	41.0	0.22915	0.00095
300	51.5	0.31426	0.00105
360	60.0	0.39794	0.00111
420	68.4	0.50031	0.00119
480	74.5	0.59346	0.00124

TABLE XIII.

200 Grams Solution. $A = 99.5$.

0	0	.....	.....
30	9.0	0.04117	0.00137
60	20.2	0.09855	0.00164
120	37.0	0.20194	0.00168
180	52.7	0.32757	0.00182
240	66.5	0.47931	0.00199
300	77.9	0.66337	0.00221
360	86.0	0.86745	0.00241

TABLE XIV.

300 Grams Solution. $A = 97.4$.

0	0	.....	.....
60	28.9	0.15287	0.00254
105	46.9	0.28527	0.00262
150	60.4	0.42036	0.00280
195	72.4	0.59162	0.00303
240	81.4	0.78444	0.00326
285	87.4	0.98856	0.00347
330	91.9	1.24820	0.00378

TABLE XV.

400 Grams Solution. $A = 98$.

t.	x.	$\log \frac{A}{A-x}$.	$\frac{1}{t} \log \frac{A}{A-x}$.
0	0	.....	.....
15	10.5	0.04922	0.00328
45	28.0	0.14613	0.00325
75	43.5	0.25483	0.00339
120	61.5	0.42894	0.00357
170	78.0	0.69020	0.00406
215	87.0	0.94984	0.00442
240	91.0	1.14623	0.00477

A consideration of the above figures shows at once that the hypothesis regarding the nature of the reaction is not the right one, as the speed increases regularly from the beginning to the end. In other words, the speed is an accelerated one, and the cause of this acceleration may be found in the sulphuric acid liberated as the reduction advances. The acid liberated is proportional to the ferric salt reduced, and may be measured, therefore, by x.

It is evident also from the tables that the speed of the reaction varies with the amount of sugar in the solution, as it is almost four times as great with the 400 grams solution as with the 100 grams solution. In any one experiment, however, this sugar amount may be considered as remaining practically constant, and a new equation expressing the speed may now be written with two terms:

$$\frac{dx}{dt} = K(B+x)(A-x),$$

in which B represents amount of sugar.

This on integration yields:

$$Kt = \frac{1}{A+B} \log \frac{B+x}{A-x} + \text{Cons.}$$

As $x = 0$ for $t = 0$, we have for the definite integral:

$$Kt = \frac{1}{A+B} \log \frac{(B+x)A}{(A-x)B}.$$

Before this formula can be used for practical calculations some numerical value must be given to B. From preliminary tests referred to above, it appears that the sugar amount is prob-

ably a little low in the weakest solution and high in the strongest to be considered chemically equivalent to A. However, for simplicity in calculation, it may be assumed that A and B are equal, when our formula becomes:

$$K = \frac{1}{2At} \log \frac{A+x}{A-x}.$$

On this assumption the tables below have been calculated. For the 100 grams sugar solution the value of K for $B = 0.75\ A$ is added in the last column, and for the 400 grams solution the value for $B = 2A$.

TABLE XVI.

100 Grams Solution. $A = 100$.

t.	x.	$\frac{1}{2A} \log \frac{A+x}{A-x}$.	$\frac{1}{2At} \log \frac{A+x}{A-x}$.	$\frac{1}{t(A+B)} \log \frac{A(B+x)}{B(A-x)}$
0	0	.....	.....	.....
90	14.0	0.000612	0.00000679	0.00000888
180	30.5	0.001385	0.00000760	0.00000969
240	41.0	0.001892	0.00000788	0.00000996
300	51.5	0.002473	0.00000824	0.00001031
360	60.0	0.003010	0.00000836	0.00001037
420	68.4	0.002632	0.00000865	0.00001064
480	74.5	0.004176	0.00000820	0.00001063
			0.00000802	

TABLE XVII.

200 Grams Solution. $A = 99.5$.

0	0	.....	.....
30	9.0	0.000395	0.00001319
60	20.2	0.000896	0.00001497
120	37.0	0.001704	0.00001420
180	52.7	0.002573	0.00001430
240	66.4	0.003525	0.00001469
300	77.9	0.004595	0.00001532
360	86.0	0.005718	0.00001586
			0.00001465

TABLE XVIII.

300 Grams Solution. $A = 97.4$.

0	0	.....	.....
60	28.9	0.001364	0.0000227
105	46.9	0.002340	0.0000223
150	60.4	0.003233	0.0000215
195	72.4	0.004271	0.0000218
240	81.4	0.005381	0.0000224
285	87.4	0.006502	0.0000228
330	91.9	0.007888	0.0000239
			0.0000225

TABLE XIX.

400 Grams Solution. $A = 98$.

t.	x.	$\frac{1}{2A}\log\frac{A+x}{A-x}$	$\frac{1}{2At}\log\frac{A+x}{A-x}$	$\frac{1}{t(A+B)}\log\frac{A(B+x)}{B(A-x)}$
0	0	.....	.....	.....
15	10.5	0.000477	0.0000317	0.0000163
45	28.0	0.001302	0.0000289	0.0000154
75	43.5	0.002114	0.0000282	0.0000155
120	61.5	0.003267	0.0000272	0.0000155
170	78.0	0.004819	0.0000283	0.0000167
215	87.0	0.006254	0.0000291	0.0000175
240	91.0	0.007303	0.0000304	0.0000185
			0.0000291	

It appears from the above tables that the constants calculated from the simple formula, with $A = B$, are somewhat more regular than those from the other. In the first experiment, with the 100 grams solution, the reaction was not complete, and the results are at best unsatisfactory. But in the others these mean values for the speed

0.0000146
0.0000225
0.0000291

stand to each other almost exactly in the relation 2 : 3 : 4, showing the close relation of speed to dissolved sugar. In each series the values for K are as uniform as could be expected, and show that the formula chosen represents the reaction very well.

CHICAGO. JULY 3, 1897.

THE EXACT ESTIMATION OF TOTAL CARBOHYDRATES IN ACID HYDROLYZED STARCH PRODUCTS.

BY GEO. W. ROLFE AND W. A. FAXON.

Received June 11, 1897.

THE determination of the exact amount of carbohydrates present in solutions of commercial glucose has always been conjectural, since the evaporation method, the only available means of estimation, has always caused in the residue an intermediate amount of decomposition, usually attributed to oxidation or the destructive effect of high temperature. Since, however, in acid hydrolyzed starch products, it seems certain that the component carbohydrates preserve their individuality

throughout the combinations which they may make with each other, at least so far as to have constant optical and chemical properties, as well as a constant influence on the specific gravity per unit weight of each present in solution, it is quite possible to determine the *proportional amount* of each constituent by the use of one arbitrary specific factor throughout the calculation. This has been explained in detail in several publications of O'Sullivan, Brown, Heron, Morris, and others. It is also well known that the factor used is that representing the increase in specific gravity caused by one gram of cane sugar in 100 cc. of solution.

It follows that if the specific gravity influences of the isolated carbohydrates were known it would be quite possible to predict the specific gravity factor of any hydrolyzed starch product. A year ago an attempt was made by one of us to predict these factors of the hydrolyzed starch products for all rotation between the limits of possible specific rotatory powers for the factor 386. A provisional curve was plotted from the following formula :

$$\Sigma = m\Sigma_m + g\Sigma_g + d\Sigma_d.$$

Σ being the specific gravity factor of the hydrolyzed starch product identified by its specific rotatory power ; m, g, and d, the respective percentages of maltose, dextrose, and dextrin present ; and Σ_m, Σ_g, Σ_d, their corresponding specific gravity factors.

We considered this curve a provisional one, as we were obliged to approximate the factor for dextrin from the imperfect data of O'Sullivan, Salomon, and others, taking 0.00400 as the most probable value. The factors for dextrose and maltose were those of Salomon[1] for ten per cent. solutions, 0.00381 and 0.00390, respectively. We found that the plotted values of the calculated factors, where the specific rotatory powers were expressed as abscissae, formed a *straight line joining the plots corresponding to the factors taken for pure dextrin and dextrose* at the corresponding rotation of 195° and 53.5°.

Having defined approximate theoretical values we have sought to confirm them by actual determinations of the total solids present in a number of representative solutions prepared as previously described.[2]

[1] *J. prakt. Chem.*, **2**, 28.
[2] This Journal, **18**, 871–872.

Much ingenious apparatus[1] has been devised for overcoming the decomposition in drying already referred to. The principles of one class is the introduction of a presumably inert atmosphere, such as coal gas or hydrogen. Another class uses a vacuum, which mitigates at the same time oxidation and influence of high temperature.

Apparently, experience places so little confidence in the advantages of any of these multifarious appliances, at least in the case of sugars, that the ordinary method of drying at about 100° till the continual loss does not exceed a given rate per hour, is that usually recommended. We therefore at first dried ten cc. each of solutions of hydrolyzed starch products on paper rolls at 105°–110° C.,[2] the rolls being placed in weighing beakers, and dried to practically constant weight in an oven kept at the given temperature. The results obtained were discordant, and in general lower than those of our provisional curve.

A second series of determinations were made by drying paper rolls, prepared in a similar way, in a vacuum pan, the temperature being about 40°. In breaking the vacuum, air was passed through sulphuric acid and made to enter at the bottom of the pan to avoid the descent of moist vapors. Drying by this method was exceedingly tedious, and the values obtained are much lower than given by our assumed curve, besides being discordant. They indicate the need of more heat in drying.

At this point in our work we received the important paper by Brown, Morris, and Millar,[3] giving the details of an elaborate investigation of the primary carbohydrates and of the products of diastase hydrolysis. In the latter the actual values were successfully predicted by a method similar to ours, but by a somewhat more exact formula, as it took into consideration variations in the factors due to those of concentration. These investigators used the drying apparatus designed by Lobray de Bryn and Von Laent[4] for the drying of maltose. This apparatus had worked so successfully for diastase converted solutions that we at once adopted a modification of it for our next essay. Several pieces of apparatus of the type described below (Fig. 1) were

[1] Wiley's Principles and Practice of Agricultural Analysis, Vol. 3; see also recent bulletin by the U. S. Department of Agriculture.

[2] Rolfe and Defren : this Journal, **18**, 872.

[3] *J. Chem. Soc., Jan., 1897.*

[4] *Rec. Trav. Chim., 1894*, **13**, 218.

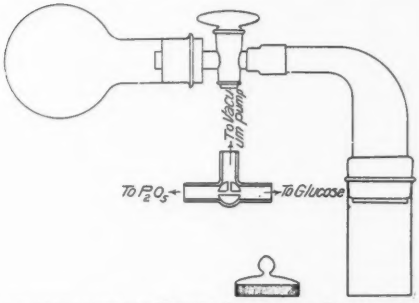


FIG. 1.—APPARATUS FOR DRYING SUGARS AND GLUCOSE SYRUPS.

improvised from the stock of material available. Our apparatus is arranged so that the greater bulk of the water can be first removed without coming in contact with the phosphorus pentoxide. This avoids previous evaporation on a water-bath. The tared weighing beaker containing the solution to be evaporated is slipped on the end of the adapter, an air-tight joint being made with "bill-tie" tubing. By the three-way stop-cock, communication can be had with the vacuum pump and with a 250 cc. flask containing phosphorus pentoxide, or either can be shut off.

The method of drying is as follows: The cock is opened to the pump only, and the air exhausted to 680–690 mm. The beaker is lowered into an oil-bath and heated to about 100° till most of the water is evaporated. Communication is then made with the pentoxide flask, and the mass dried to constant weight at about 120°. For convenience, the vapor from the various pieces of apparatus were passed through a four-liter vacuum pan. This large receiver produced an almost instantaneous exhaustion when a stop-cock was opened. Complete drying usually required from eighteen to twenty-four hours. The slowness of our drying apparatus was possibly due to the contracted opening through the stop-cock, which may have prevented free circulation of vapors over the pentoxide. This drawback was the result of the necessary improvising of our apparatus from stock at hand.

The results obtained are tabulated in the following table, and

also plotted in Fig. 2. As will be seen they form a straight line

TABLE.

No.	Time drying. Hours.	Vol. of solution. cc.	$d_{15.5}$.	α_{D386}.	Weight of residue.	Factor obtained.	Factor calculated.
1	18	10	1.02835	164.2	0.7104	0.003992	0.003980
2	18	10	1.03134	160.0	0.7833	0.003999	0.003974
3	24	10	1.03657	144.8	0.9223	0.003965	0.003954
4	18	10	1.03364	141.8	0.8509	0.003954	0.003950
5	24	10	1.04212	138.7	1.0644	0.003957	0.003946
6	18	10	1.03650	136.1	0.9222	0.003953	0.003942
8	18	10	1.03701	128.0	0.9376	0.003943	0.003931
9	24	10	1.03701	128.0	0.9417	0.003930	0.003931
11	18	10	1.03841	115.7	0.9781	0.003927	0.003918
12	18	10	1.03704	111.7	0.9454	0.003918	0.003911
13	18	10	1.03704	111.7	0.9465	0.003914	0.003911
15	24	10	1.03843	104.7	0.9827	0.003910	0.003901
16	18	10	1.03545	90.5	0.9127	0.003885	0.003883
17	18	10	1.03594	81.3	0.9282	0.003883	0.003871
18	18	10	1.03549	73.4	0.9162	0.003870	0.003860
19	18	10	1.03881	70.5	1.0081	0.003850	0.003856

(The omitted numbers are those of samples which were lost by breakage, or scorching due to loss of vacuum.)

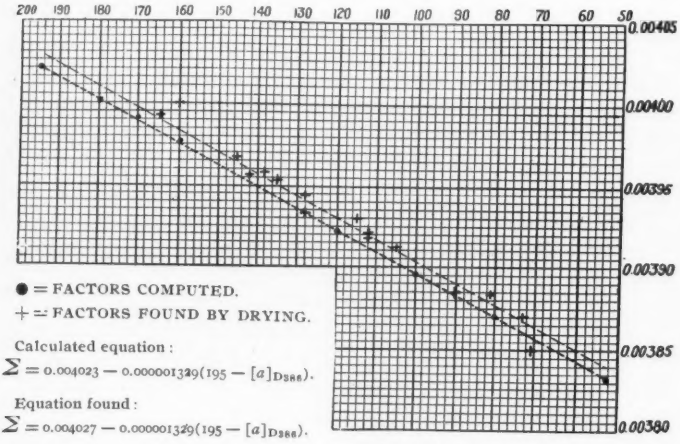


FIG. 2.—SPECIFIC GRAVITY FACTORS FOR APPROXIMATELY TEN PER CENT. SOLUTIONS OF HYDROLYZED STARCH PRODUCTS.

which is very slightly higher than the line calculated by using the revised carbohydrate value of Brown, Morris, and Millar.

The variation is very slight, as the plot is drawn on a scale by which one division represents about 0.06 per cent. of the values obtained. The two equations obtained are more nearly concordant when we take into consideration that the average of the specific gravities of the samples is about 1.0360. This would raise the calculated value 0.000003 on the scale, or a little more than one half of a division. We, therefore, have adopted as the most probable values what happens to be the mean. Our conclusion, then, is that within the concentrations expressed by the specific gravity factors, 1.035 and 1.045, we can calculate the absolute specific gravity influence of any acid hydrolyzed starch solution by the equation, $\Sigma = 0.004023 - 0.0000001329(195 - [\alpha]_D)$, when the specific rotatory power (obtained by the factor 0.00386) is known. These values within the limits of concentration given are correct to less than two-tenths per cent. of their values. For commercial glucoses, the factor 0.00393, taken as a constant, is sufficiently exact for most determinations.

While this equation will now enable us to determine the exact amount of carbohydrate in solution when the specific gravity has been previously corrected for the influence of other dissolved material, the simpler computation based on the factor 0.00386 will doubtless continue in use as more convenient for those calculations where proportion of carbohydrates is alone desired.

We have also under investigation the action of heat on commercial glucoses when samples are boiled down to candies, as well as the study of certain disturbing influences on the determination of cupric reducing powers of glucoses. The results are not yet complete enough for publication.

A FURTHER COMMUNICATION ON THE ESTIMATION OF PHOSPHORIC ACID BY TITRATION OF THE AMMONIUM PHOSPHOMOLYBDATE PRECIPITATE WITH STANDARD ALKALI.

By B. W. Kilgore.

Received June 17, 1897.

DURING the past four years the writer has done a great deal of work on this method,[1] and the results obtained in this laboratory for the past two years, at least, by five analysts,

[1] Bul. 43 and 47, pp. 68–104 and 62–83, Chem. Div., U. S. Department of Agriculture; Bul. 119, North Carolina Experiment Station: and this Journal, 16 and 17, Nos. 11 and 12.

warrant us in considering it thoroughly accurate and reliable. More recently the method has been extensively and successfully employed in experiment station and other laboratories. Some chemists, however, have not been able to get uniformly good results with it. These appear to be mostly those who have worked the method but little, while the difficulty with others seems to be due to a misunderstanding as to how the method should be carried out.

At the last meeting of the Association of Official Agricultural Chemists, two main objections were brought against its adoption as an official method at that time. One was that it had not been tried upon a sufficient variety of fertilizers and fertilizer materials used in the trade to show that it would give as good results on all of them as it had upon those it had been worked upon, when in the hands of those who had worked the method to any extent.

The other objection was that brought out in the paper[1] of Mr. T. S. Gladding. Mr. Gladding had made twenty-two comparative tests of the volumetric method with the official gravimetric method and his gravimetric method on a microcosmic salt and various fertilizers with closely agreeing results in all cases. He then turned over a set of precipitates to an assistant to filter and wash free of acids, according to the method. It was found that the precipitates could not be freed from acid; and upon closer examination it was observed that the water was dissolving the precipitate.

The experiments, the results of which follow in the table, were planned to throw light upon, and if possible to settle, these two questions.

[1] Bul. 49, Chem. Div., U. S. Department of Agriculture, p. 75.

COMPARATIVE PHOSPHORIC ACID RESULTS ON VARIOUS FERTILIZER MATERIALS BY GRAVIMETRIC AND VOLUMETRIC METHODS.

Materials.	Gravimetric method.	Volumetric method.	Washed with water.	Washed with three per cent. ammonium nitrate solution.	Washed with three per cent. potassium nitrate solution.	Amount of solution corresponding to 2 grms substance used in volumetric method.
	Per cent.	Per cent.	Cc.	Cc.	Cc.	Grams.
1. Cottonseed meal....	2.97	2.97	200	...	...	0.2
	...	2.93	500	...	...	0.2
	2.96	2.91	500	...	...	0.2
2. Tankage	11.62	11.68	200	...	...	0.2
	11.67	11.58	500	...	...	0.2
	....	11.60	...	200	...	0.2
	....	11.45	...	500	...	0.2
3. North Carolina phosphate	18.27	18.20	200	...	...	0.2
	18.27	18.20	500	...	...	0.2
	....	18.18	...	200	...	0.2
	....	17.88	...	500	...	0.2
4. South Carolina phosphate	27.98	28.06	200	...	...	0.2
	27.98	28.09	500	...	...	0.2
	....	28.04	...	200	...	0.2
	....	27.74	...	500	...	0.2
5. Pennsylvania phosphate	18.59	18.59	200	...	...	0.2
	18.58	18.56	500	...	...	0.2
	....	18.56	...	200	...	0.2
	....	18.34	...	500	...	0.2
6. Thomas slag (American).....	*a* 16.38	16.05	200	...	...	0.2
	a 16.43	16.00	500	...	...	0.2
	b 16.14	15.98	...	200	...	0.2
	c 16.04	15.75	...	500	...	0.2
7. Thomas slag (European).....	*a* 18.15	17.98	200	...	...	0.2
	a 18.08	17.97	500	...	...	0.2
	c 17.90	17.88	...	200	...	0.2
	....	17.73	...	500	...	0.2
8. Bone meal.....	22.14	22.10	200	...	...	0.2
	22.02	22.08	500	...	...	0.2
	....	22.00	...	200	...	0.2
	....	21.95	...	500	...	0.2
9. Acid phosphate	17.44	17.56	200	...	...	0.2
	....	17.51	500	...	...	0.2
	....	17.51	...	200	...	0.2
	....	17.30	...	500	...	0.2

Materials.	Gravimetric method.	Volumetric method.	Washed with water.	Washed with three per cent. ammonium nitrate solution.	Washed with three per cent. potassium nitrate solution.	Amount of solution corresponding to grms substance used in volumetric method.
10. Mixed fertilizer	10.23	10.40	200	...	...	0.2
	10.25	10.35	500	...	...	0.2
11. Tennessee phosphate (low grade).....	23.08	23.11	200	...	...	0.2
	....	23.11	500	. .	..	0.2
12. Tennessee phosphate (high grade).....	35.07	35.00	200	...	...	0.1
	34.85	35.00	500	...	...	0.1
13. Aluminum phosphate	46.91	47.10	200	...	...	0.1
	46.82	47.20	500	...	...	0.1
	47.00	....	...	...	...	.
14. Florida phosphate..	37.74	37.80	200	...	...	0.1
	37.62	37.78	500	...	...	0.1
15. Sodium phosphate..	19.97	19.96	200	...	...	0.2
	20.07	19.90	500	...	...	0.2
	20.03	19.76	...	...	200	0.2
	19.97	18.68	...	...	500	0.2
	19.82	19.90	...	200	...	0.2
	....	19.82	...	500	...	0.2

Sample No. 6, American Thomas slag, contained a very large amount of iron, while No. 7, European slag, contained considerable iron. "*a*" were precipitated only once with molybdic solution, and the "white" precipitates were contaminated with iron. "*b c*" were precipitated twice with molybdic solution to get rid of iron." The "white" precipitates giving results "*c c*" were free from iron, but "*b*" still contained a very small amount.

Note.—The solutions used in this work were the same as those given in the description of the method in Bul. 46, Div. Chem., U. S. Department of Agriculture, p. 13.

With reference to the variety of materials, an examination of the publications referred to at bottom of page 703, under reference (1), will show that the method has already been worked upon quite a variety of fertilizer materials and mixed goods, which with the materials investigated in this paper, appears to include nearly all, if not all, the sources of phosphoric acid in the fertilizer trade. Besides these, the large number of results presented to the Association last year by Mr. John P. Street, and

published in the Annual Report of the New Jersey Station,[1] shows that the method gives good results on mixed goods. Mr. Street says: "The materials analyzed included 276 samples of complete fertilizers, of varying composition and origin; and are believed to fairly represent the average goods on the market at the present time. The results secured were extremely satisfactory, the average results by the volumetric method being 10.72 per cent. against 10.70 per. cent. by the official method. Of these results, 150 were higher by the volumetric, 113 lower, and thirteen identical with the official method; the greatest variation was 0.16 per cent., and 114 samples varied less than 0.05 per cent.

The results obtained by both the gravimetric and volumetric methods on the samples reported upon in this paper show good agreement, except those on samples 6 and 7, American and European manufactured Thomas slags. The American slag contained a very large amount of iron, and the European one quite a considerable quantity. When the yellow precipitates from these samples were dissolved on the filter with dilute ammonia water considerable iron remained on the filter. The results marked "*a*" in the table were secured by carrying these through according to the usual custom without reprecipitating to get rid of iron. These "*a*" results are about 0.40 per cent. higher than the corresponding volumetric ones on the American slag, and considerably higher on the European one. The "white" precipitates giving these high results were seen by color and shown by chemical test to contain iron. A second set of determinations was then made, using the same solutions from which the above results were obtained and precipitating twice with molybdic solution to get rid of iron, when results "*c*, *c* and *b*" were secured. These results show close agreement with the volumetric ones. Result "*b*" still contained a small amount of iron.

It appears then that the volumetric method has not only given as good results on all the samples here worked, including the *very high percentages*, as the gravimetric method, but on the samples containing large amounts of iron the results were better. I might state in this connection that we have found the

[1] 17th Annual Report, p. 118.

volumetric method to give very satisfactory results in estimating the phosphoric acid in soils, where a large amount of iron is usually present.[1]

Now as to Mr. Gladding's point of telling when the precipitate has been washed sufficiently. It might be stated here also that others have had difficulty at this point and the statement in the method as published in Bulletin 46, Chemical Division, United States Department of Agriculture. p. 14, to wash the precipitate "till no longer acid" is responsible to some extent at least for this trouble.

It is well known that ammonium phosphomolybdate is slightly soluble in water and is an acid salt; and it would therefore be impossible to get a filtrate from washing with water that would be strictly neutral to very delicate indicators, like phenol phthalein. It will be found, however, that when the filtrate is allowed to drop from the neck of the funnel upon delicate litmus paper, that the wash water will be neutral to litmus after 100 to 200 cc. water has passed through. The work here reported and that previously done by us,[2] together with the work of Street,[3] McDonnell, and others, shows that 150 to 250 cc. water, and often less, has been sufficient in all cases to free the precipitates of acid. But as stated by the writer in a previous paper on washing the yellow precipitate, "there is danger, however, of mechanical loss. The precipitate is first washed by decantation with dilute nitric acid and potassium nitrate, and afterwards with water to remove the nitric acid. It is in this after washing, when all the salts have been removed from the precipitate and as much as 600 to 700 cc. of water has been used, the precipitate begins to pass through the filter mechanically and settle to the bottom of the receptacle. We have not, however, found it necessary to wash with more than 300 cc. water."[4] Perhaps this will explain the difficulty which occurred in Mr. Gladding's laboratory, in that more water was used for washing than was necessary. When these large quantities of water are used the precipitate not only gets through the filter and settles out in

[1] Bul. 47, Chem. Div., U. S. Department of Agriculture, p. 82.
[2] Bul. 47, Chem. Div., U. S. Department of Agriculture, p. 62.
[3] Seventh Annual Report, New Jersey Station, p. 118.
[4] This Journal, 17, 958.

the filtrate but it dissolves far more readily then than when smaller amounts of water are used for washing.

In the light of the experience of the past three years, however, it does not now seem to be necessary to wash with more than 150 to 200 cc. of water, and the smaller of these is not much more, if any, than is used in washing the yellow salt in the gravimetric method.

In the results which precede in the table, I have made an additional test of the washing question by using 200 cc. and 500 cc. of water and the wash solutions, and making the determinations side by side and from the same solutions. The gravimetric results used for comparison were obtained on the same solutions as the volumetric ones. The results show that 200 cc. of water, even with these *very high percentages*, was sufficient in all cases, and that 500 cc. only lowered the results slightly when at all. When 200 cc. of three per cent. ammonium and potassium nitrate solutions were used for washing the results were practically the same as those obtained when the two quantities of water were used, but when they were increased to 500 cc. the results, greatly to my surprise, were much lower. The results were so much of a surprise that quite a number of them were repeated, and while they were not uniform in all cases, they were always low. We had hoped to be able to wash with a very large volume of ammonium nitrate solution without appreciably dissolving the precipitate or causing it to run through the filter. The filtrates from these 500 cc. ammonium and potassium nitrate washes were perfectly clear, but on evaporation the ammonium phosphomolybdate was found to be in solution.

In these determinations three-inch Hirsch funnels, with disks of filter paper covering the bottoms, and right strong suction, were used in filtering. The filtrates were not tested, but other determinations on the same sample by using ordinary funnel and filter paper without pressure showed them to be free of acid, after washing with 150 to 200 cc. of water. These results agreed well with those obtained with the pump. All the precipitates were washed twice by decantation with dilute nitric acid and once with potassium or ammonium nitrate solution before washing with water.

In view of the results with potassium and ammonium nitrate

solutions it is suggested that one washing by decantation with water take the place of washing with potassium nitrate, following the washing with dilute nitric.

A word may not be out of place here in regard to the titration and end reaction. The greater the amount of yellow precipitate present the more slowly does the phenolphthalein color disappear, but up to twenty per cent. or more, when two-tenths gram of substance is used, the end reaction is quite sharp. For percentages much above twenty I consider one-tenth gram substance better to use, when the end reaction will be found sharp for any percentages one will be called upon to work. To summarize: For percentages below five use four-tenths gram substances (or about); for percentages between five and twenty use two-tenths gram, and above twenty use one-tenth gram.

It will also be found that by adding the indicator after the precipitate has been dissolved in the alkali, that the molybdenum colorations which sometimes interfere with the end reaction will be avoided. This observation was made by Street in his work previously referred to, and my observations corroborate it. Of the results presented in the table, the gravimetric determinations were made by Messrs. W. M. Allen, H. K. Miller, and myself; and the volumetric ones by myself.

The volumetric method was somewhat modified at the last meeting of the Association of Agricultural Chemists, and in such a way as to get around the difficulty of excessive washing spoken of in this paper. I repeat here the method in the form it was recommended that it should be tested in the work of this year:

Dissolve two grams substance in nitric and hydrochloric acids, incinerating beforehand to destroy organic matter if necessary, and make up to volume of 200 cc. For percentages below five use forty cc. of solution, for percentages between five and twenty use twenty cc. (and for percentages above twenty use ten cc.); add five to ten cc. concentrated nitric acid, nearly neutralize with ammonia, heat in the water-bath at 60°–65° C., add fifty cc. freshly filtered molybdic solution for each one-tenth gram phosphorus pentoxide present, and digest in water-bath for ten to fifteen minutes.

Decant the clear liquid on the filter as quickly as possible,

using Hirsch funnel with suction or ordinary funnel and filter paper with or without pressure; wash the precipitate by decantation twice with sixty per cent. nitric acid solution, using about fifty cc. of the solution each time, agitating thoroughly, and allowing the precipitate to completely settle, once with the same amount of three per cent. ammonium or potassium nitrate solution,[1] transfer it to the filter, and wash it five or six times with water, using 150 to 250 cc.[2] Now wash the filter and contents back into the beaker, add excess of standard alkali, and then a few drops of phenolphthalein, and titrate back with standard nitric acid.

THE ACTION OF NITRIC ACID UPON ALUMINUM AND THE FORMATION OF ALUMINUM NITRATE.

By Thomas B. Stillman.

Received July 17, 1897.

THE bibliography of aluminum, in reference to the action of nitric acid upon the metal, is well worthy of investigation. The statements are so conflicting, even in the recent literature bearing upon this subject, that direct experimentation was required to demonstrate the solubility of aluminum in nitric acid.

Wöhler[3] states: "Aluminium is not attacked by $HNO_3 + Aq$ even when concentrated and boiling.[4]

Deville[5] gives as the result of his experiments that aluminum is not attacked by boiling nitric acid, dilute or concentrated.

Richards[6] refers to the statement of Deville, but also adds: "In boiling acid solution takes place, but with such slowness that I had to give up this mode of dissolving the metal in my analysis." "By cooling the solution all action ceases."

Buff and Heeren[7] coincide with Deville, "Aluminium wird weder von verd. noch konz. HNO_3 angegriffen."

Montemartin,[8] "Aluminium is slowly soluble in 27 per cent.

[1] It is suggested that water be used for this washing by decantation instead of the nitrate solution.

[2] In our experience 200 cc. of water is sufficient.

[3] *Pogg. Ann.*, **2**, 223.

[4] A Dictionary of Chemical Solubilities, by Comey, *1896*.

[5] *Compt. Rend.*, **38**, 279.

[6] Aluminium, its Properties, Metallurgy and Alloys, by J. W. Richards, *1890*.

[7] Handbuch der anorganische Chemie, Dammer, **2**, 86, *1894*.

[8] *Gazz. Chim. Ital.*, **22**, 397.

HNO_3 + Aq., 100 cc. HNO_3 + Aq. requiring 2 months to dissolve 2 grams of aluminium."[1]

M. M. Pattison Muir[2] states, in relation to the chemical properties of aluminum: "It is scarcely attacked by HNO_3+Aq."

Weeren,[3] "Aluminium is soluble in HNO_3 + Aq *in vacuo*."

Storer's Dictionary of Solubilities of Chemical substances, page 28, gives the one reference only regarding the action of nitric acid upon aluminum, *viz.*, "unacted upon by nitric acid, either concentrated or dilute, at ordinary temperatures, but is slowly dissolved therein on boiling."

N. Menschutkin,[4] "Nitric acid has only a slight action upon aluminium, the layers of nitric oxide formed protecting the metal from further attack."

Ira Remsen,[5] "At ordinary temperatures nitric and sulphuric acids do not act upon aluminium; at higher temperatures, however, action takes place."

Birnbaum,[6] Concentrated and dilute nitric acid, either cold or warm, are without action upon aluminum. ("Concentrirte und verdünnte Salpetersäure sind in der Kälte und Wärme ohne Wirkung auf Aluminium.")

W. Borchers,[7] Nitric acid is almost without action upon aluminum. ("Salpetersäure ist fast ganz unwirksam auf Aluminium.")

Ferdinand Fischer,[8] "Nitric acid and sulphuric acid scarcely affects aluminium."

J. Arthur Phillips,[9] "Aluminium is not attacked by cold nitric acid, and only slowly on boiling."

Ad. Wurtz,[10] "Nitric acid, dilute or concentrated, has no effect upon aluminium at ordinary temperatures. On boiling, however, solution of the metal is effected with extreme slowness."

[1] A Dictionary of Chemical Solubilities, by Comey, 3.
[2] Watt's Dictionary of Chemistry, 1, 142, (latest edition).
[3] *Ber. d. chem. Ges.*, **24**, 1798.
[4] Analytical Chemistry, by N. Menschutkin, London, *1895*, p. 64.
[5] Inorganic Chemistry, by Ira Remsen, N. Y., *1895*, p. 452.
[6] Handworterbuch der Chemie, Fehling, 1, 339.
[7] Lexicon der gesamten Technik, Leuger, Leipzig, *1896*, 1, 262.
[8] Manual of Chemical Technology, (Wagner), 13th German edition as remodelled by Dr. Ferdinand Fischer, p. 223.
[9] Elements of Metallurgy, by J. Arthur Phillips and H. Bauermann, 528.
[10] Dictionnaire de Chemie, 1, 167.

Alfred E. Hunt, John W. Langley, Charles M. Hall,[1] "Aluminium is unaffected by either concentrated sulphuric or nitric acids."

Encyclopedia Britannica, **1**, 647, states: "Aluminium is not attacked by nitric acid, even when the acid is concentrated,"

Charles M. Hall,[2] "Sulphuric and nitric acids act upon aluminium with extreme slowness, not dissolving it appreciably after several days' exposure to their action."

Henry Roscoe,[3] Sulphuric and nitric acids, both dilute and concentrated, have no effect upon aluminium."

Hanford Henderson,[4] "Aluminium is almost untouched by nitric and sulphuric acids."

G. A. Leroy,[5] Sulphuric and nitric acids act immediately upon aluminium. "(Schwefelsäure und salpetersäure griefen das aluminium schnell an.")

R. L. Packard[6] gives a résumé of the experiments of LeRoy as follows: "LeRoy used aluminium foil having the composition of 98.28 per cent. to 99.60 per cent. aluminium; 1.60 per cent. to 0.30 per cent. iron; 0.25 per cent. to 0.10 per cent. silicon.

The foil was polished, freed from fat with caustic soda, washed with alcohol, dried in the air-bath, cut up, weighed and introduced into the acids.

	Temperature.	Aluminum dissolved in grams per sq. meter in 12 hours.
Pure HNO_3, sp. gr. 1.383····	15°–20° C.	17.0 grams.
Common HNO_3, sp. gr. 1.332	15°–20° C.	16.3 grams.
Pure HNO_3, sp. gr. 1.382····	100° C.	Violent action.

According to these results, almost pure aluminum, 99.5 per cent., is attacked even in the cold by nitric acid.

Very elaborate experiments were made by G. Lunge and E. Schmid[7] regarding the action of nitric acid upon aluminum. They show that aluminum is readily attacked by nitric acid of 1.20 sp. gr. at ordinary temperatures, and that with nitric acid of sp. gr. 1.50 the action is comparatively feeble.

[1] The Properties of Aluminium, wih Some Information Relating to the Metal. Trans. Amer. Mining Engineers, **18**, 537.

[2] The Properties of Aluminium. Electrical World, **17**, 390.

[3] Aluminium. Nature, **40**, 185.

[4] Aluminium. *J. Frank. Inst.*, **126**, 293.

[5] Action of Sulphuric and Nitric Acids upon Aluminium. *Chem. Ztg.*, Repert., **15**, 276; Bull. Rouen, **19**, 232.

[6] Bull. U. S. Geological Survey, 1893; This Journal, **15**, 221.

[7] *Ztschr. angew. Chem.*, *1892*, 7.

The following table shows the results of the action of various strengths of nitric acid upon aluminum foil at ordinary temperature (20° C.); duration of test being ten days.

Specific gravity of nitric acid.	Experiment I. Milligrams aluminum dissolved from 60 sq. centimeters.	Experiment II. Milligrams aluminum dissolved from 60 sq. centimeters.	Average. Milligrams aluminum dissolved from 60 sq. centimeters.	Average. Milligrams aluminum dissolved from 100 sq. centimeters.
1.20	615.0	617.7	616.4	1027.4
1.40	242.7	236.9	239.8	399.7
1.50	23.7	21.6	22.7	37.8

These experiments were conducted in the chemical laboratory of the Zurich "Polytechnicum."

The aluminum was in the form of sheet metal, cut into strips of eighty mm. long, twenty-seven mm. wide, and one mm. thick. Its composition was: Aluminum 99.2 per cent., iron 0.25 per cent., combined silicon 0.44 per cent., and crystallized silicon 0.11 per cent.

Messrs. Lunge and Schmid conclude as follows:

"Several experiments made by us convince us that the statements in the text-books, according to which aluminum is slightly or not at all attacked by HNO_3, are decidedly incorrect; which fact brings to naught the hope entertained that this metal can be used in the manufacture of nitric acid."

In confirmation of these tests I made the following experiments, using aluminum (manufactured by the Pittsburg Reduction Co.) containing 99.6 per cent. of aluminum.

Coarse turnings were made of the metal, and six samples, each of one gram, were transferred to glass flasks and treated as follows:

EXPERIMENT I.

Specific gravity of nitric acid	1.15
Amount of acid taken	100 cc.
Length of test	7 days
Temperature of acid	20° C.
Per cent. of aluminum dissolved	94.2

I. Result = 94.2 per cent. aluminum dissolved.

EXPERIMENT II.

Specific gravity of nitric acid	1.15
Amount of acid taken	100 cc.
Length of test	20 minutes
Temperature of acid	100° C.
Per cent. of aluminum dissolved	100

II. Result = 100 per cent. aluminum dissolved.

EXPERIMENT III.

Specific gravity of nitric acid	1.35
Amount of acid taken	100 cc.
Length of test	7 days
Temperature of acid	20° C.
Per cent. of aluminum dissolved	89

III. Result = 89 per cent. aluminum dissolved.

EXPERIMENT IV.

Specific gravity of nitric acid	1.35
Amount of acid taken	100 cc.
Length of test	30 minutes
Temperature of acid	100° C.
Per cent. of aluminum dissolved	100

IV. Result = 100 per cent. aluminum dissolved.

EXPERIMENT V.

Specific gravity of nitric acid	1.46
Amount of acid taken	100 cc.
Length of test	7 days
Temperature of acid	20° C.
Per cent. of aluminum dissolved	100

V. Result = 12 per cent. aluminum dissolved.

EXPERIMENT VI.

Specific gravity of nitric acid	1.46
Amount of acid taken	200 cc.
Length of test	2 hours
Temperature of acid	100° C.
Per cent. of aluminum dissolved	100

VI. Result = complete solution.

These results show that aluminum in the form of coarse turnings is readily acted upon by nitric acid, hot or cold, the solution of the metal being more rapid in nitric acid, of sp. gr. 1.15, than with the stronger acid of sp. gr. 1.45. In this connection, no doubt, the form in which the metal exists has a material influence upon the rapidity of solution in nitric acid.

If the metal be in thick plates the action of the nitric acid is very much retarded.

N. Menschutkin[1] considers that a layer of nitric oxide is formed, protecting the metal from further action of the acid.

To prove or disprove this statement, I selected a piece of aluminum (of the same composition as that with which the above experiments were made), one inch long, one inch wide,

[1] Analytical Chemistry, by N. Menschutkin, London, 1895, p. 65.

and one-half inch thick. This was placed in a large flask, 700 cc. of nitric acid, 1.35 sp. gr., added and kept at a temperature of 100° C., for five hours, when complete solution of the aluminum was effected. The result of these tests shows that while aluminum in thin foil, or coarse turnings, is easily dissolved in nitric acid, hot or cold, solution is materially retarded in hot nitric acid if the aluminum be present in thick plates, and that solution in cold nitric acid is practically *nil* under the same conditions.

The solution of aluminum nitrate which I obtained from experiment IV deposited crystals of aluminum nitrate in the form of colorless, truncated, rhombic, octahedral crystals, similar in composition to those described by Ordway,[1] of the composition

$$Al_2(NO_3)_6 + 18H_2O.$$

Ordway, however, obtained the aluminum nitrate by dissolving recently precipitated aluminum hydroxide in nitric acid and slowly concentrating, the crystals having the form of colorless rhombic prisms.

A. Ditte[2] describes a basic aluminum nitrate, obtained by the action of dilute nitric acid upon aluminum, of the composition $Al_2(NO_3)_2 + 4H_2O$. It exists as a white precipitate in the form of fine needles.[3]

I have failed to find in the bibliography of aluminum nitrate any reference to the formation of $Al_2(NO_3)_6 + 18H_2O$ by the direct action of nitric acid upon aluminum, as obtained in experiment IV, above described.

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[1] *Am. J. Sci.* (2), 9, 33.

[2] *Compt. rend.*, 110, 782.

[3] Handbuch der anorganische Chemie. Dammer, 3, 106.

EARLY AMERICAN CHEMICAL SOCIETIES.[1]

By H. Carrington Bolton.

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THREE chemical societies were organized in the United States before the close of the first quarter of this century; one as early as 1792, the second in 1811, and the third in 1821. These societies were short-lived, local in jurisdiction, and without much influence on the progress of the science, but it is interesting to note that professional, teaching, and amateur chemists in America formed associations for mutual improvement and for the advancement of their calling, long before their European brethren. The Chemical Society of London, the oldest in Europe, was founded in 1841, forty-nine years after the first American society; that of Paris dates back from 1858, and that of Germany from 1868. American chemists were not impelled to form independent societies owing to a lack of organizations for men of science, but they early felt the advantages of a specialized association. The society of 1792, and that of 1811, were both founded in a city honored by the presence of the venerable and dignified American Philosophical Society, established by Benjamin Franklin in 1743.

The existence of these societies has long been known, but only through casual references to them by writers on the beginnings of science in the United States; Prof. Benj. Silliman, in his essay on "American Contributions to Chemistry," read at the centennial celebration of the discovery of oxygen, held at Northumberland, in 1874, alludes to them incidentally, and Dr. Brown Goode, in his historical addresses to the Biological Society of Washington, barely mentions them.

The publications too, of the earlier societies, are very little known, being rarely found in the best libraries.

Under these circumstances it has seemed not altogether useless to summarize what information concerning these societies I have been able to gather, and to offer it as a contribution to the history of chemistry in the United States.

The three societies are:

I. The Chemical Society of Philadelphia, founded in 1792.

[1] Read before the Washington Chemical Society, April 8, 1897.

II. The Columbian Chemical Society of Philadelphia, founded in 1811.

III. The Delaware Chemical and Geological Society, founded in 1821.

I. THE CHEMICAL SOCIETY OF PHILADELPHIA.

The Chemical Society of Philadelphia was undoubtedly the earliest organized body of chemists in either hemisphere, having been "instituted" in 1792. The society does not seem to have published records of its meetings, nor of the papers presented thereat, and since at that early day the primitive local newspapers paid little attention to items of scientific interest, information concerning it is not readily obtained. I find, however, that it was flourishing in 1801–2, when it had the following officers :

President—Dr. James Woodhouse.
Vice-presidents—Felix Pascalis and John Redman.
Librarian—William S. Jacobs.
Curators—William Brown and John S. Dorsey.
Treasurer—John Y. Bryant.
Secretary—Thomas Brown.

The society held stated meetings each week.

The President of the society, Dr. James Woodhouse (1770–1809), was at the time professor of chemistry in the medical department of the University of Pennsylvania, of which he was a graduate.

This chair had been held by Dr. James Hutchinson, and on his death, in 1793, Dr. Joseph Priestley, who arrived from England a few months later, was invited to succeed him, but he declined, preferring the quiet life of Northumberland, and Dr. Woodhouse was chosen instead. Dr. Woodhouse contributed several medical papers to the New York Medical Repository, and to Coxe's Medical Museum; he also edited Chaptal's Elements of Chemistry (fourth edition, 1807, 2 vols.), and Parkinson's Chemical Pocket-Book (1802). He is said to have been the first to prove by comparative experiments the superiority of anthracite coal from Pennsylvania over bituminous coal from Virginia for intensity and regularity of heating power. (Silliman.)

The first vice-president, Felix Pascalis Ouvrière (1750–1840), had an interesting career. He was born in France, where he received his medical education; he emigrated to Santo Domingo, and while practising medicine there acquired an extensive knowledge of botany and other branches of natural history. In 1793 a revolt among the negroes compelled Pascalis to flee and he took refuge in the United States, first at Philadelphia, and later at New York, where he resided more than thirty years. He was the founder of the Linnæan Society of New York, and the author of several medical papers and reports.

The second vice-president, Dr. John Redman, (1722–1808), was a native of Philadelphia, and educated in European medical schools and hospitals. In 1786 he was made president of the Philadelphia College of Physicians. He was regarded as one of the foremost practitioners of medicine of Philadelphia, but his methods now appear super-heroic.

Dr. John Syng Dorsey (1783–1818), one of the curators, was professor of surgery and afterwards of materia medica in the University of Pennsylvania. He had a high reputation as a surgeon, but his qualifications for membership in a chemical society seem to have been based chiefly on the fact that in his youth he had attended the chemical lectures of Sir Humphry Davy (1803).

I have not found the roll of members of this early society, but it appears that Priestley, Hare, and Seybert were active in it. The ambition of the members is shown by the circumstance that in 1802 there was a standing committee prepared to "annalize every mineral production" brought before them and to give "an accurate account of each specimen free of expense."

The meeting held October 24, 1801, was made memorable by the appointment of a committee for the "discovery of means by which a greater concentration of heat might be obtained for chemical purposes." On this committee was placed among others Robert Hare, then only twenty years of age; but so soon as December 10th of the same year, he reported to the society, on behalf of the committee, his invention of the "hydrostatic" (oxy-hydrogen) blowpipe. I need not here eulogize this important and useful invention, which yielded such a fruitful harvest of discoveries. This alone justified the existence of the

first of chemical societies. In the following year the society caused Dr. Hare's account of this blowpipe to be printed in a pamphlet of thirty-four pages, 12mo., with one plate. This now rare booklet bears the title: "Memoir on the Supply and Application of the Blowpipe, containing an account of a new method of supplying the blowpipe either with common air or oxygen gas; and also of the effects of the intense heat produced by the combustion of the hydrogen and oxygen gases. Illustrated by engravings. Published by order of the Chemical Society of Philadelphia, to whom it was presented by Robert Hare, jun., Corresponding Member of the Society. Philadelphia. Printed for the Chemical Society by H. Maxwell, Columbia House, 1802."[1]

Robert Hare's subsequent career as professor of chemistry in the medical school of the University of Pennsylvania from 1818 to 1847, is well known and accessible to all inquirers.

How much longer this association of chemists continued to meet, I have not ascertained. But the work of this society was evidently remembered by those who, ten years later, founded a new one, inasmuch as they designated it by the prefix "Columbian" to avoid confusion.

II. THE COLUMBIAN CHEMICAL SOCIETY OF PHILADELPHIA.

The Columbian Chemical Society was founded in the month of August, 1811, by "a number of persons desirous of cultivating chemical science and promoting the state of philosophical inquiry." The names of the gentlemen who attended this meeting are not certainly known, but it may be presumed that they included most of those who were then elected to office; these were as follows:

Patron—Hon. Thomas Jefferson, Esq.,
President—Prof. James Cutbush,
Vice-presidents—George F. Lehman and Franklin Bache,
Secretary—John C. Heberton,
Treasurer—James J. Hamm,
Orator—John R. Barnhill,

and a "Corresponding Committee" of three: John Barnes, M.D., John Lynn, M.D., and Charles Edwards.

Thomas Jefferson's commanding position in the world of

[1] A copy of this is found in the Army Medical Library, Washington, D. C.

science and arts, as well as his literary attainments, well qualified him for the dignified office of patron. He had held the office of president of the most prominent scientific body in the United States (American Philosophical Society) for many years, and only relinquished it to accept the higher one of Chief Magistrate of the Nation. Seventeen months before the founding of the Chemical Society, Jefferson had retired from the presidency, after serving his country eight years, and was living at his country seat, Monticello.

James Cutbush, president of the Columbian Society, was at that time professor of natural philosophy, chemistry, and mineralogy at St. John's College. Little is known of his early history; in 1814 he was appointed to the army with rank of Assistant Apothecary General, and he held the position of chief medical officer of the United States Military Academy at West Point, from June, 1820, to November, 1821; the army being reorganized, he became assistant surgeon and acting professor of chemistry and mineralogy at the same institution, positions which he held until his death, December 15, 1823.

Dr. Cutbush's papers, presented to the Columbian Society, will be considered below; he published also the following: "On the Formation of Cyanogen in Some Chemical Processes Not Before Noted,"[1] "On the Composition and Properties of the Chinese Fire,"[2] "On the Composition and Properties of Greek Fire."[3] He was also the author of several books: "Useful Cabinet," (1808); "Philosophy of Experimental Chemistry," (Philadelphia, 1813), and "A System of Pyrotechny," (Philadelphia, 1825). The last named is an elaborate work of more than 600 pages, octavo.

George F. Lehman, the first vice-president, published articles in Mitchill's Medical Repository, chiefly on medical subjects.

Franklin Bache, the second vice-president, was at that date a youth of only twenty years, who had graduated at the University of Pennsylvania the year before the founding of the society. He was a grandson of Benjamin Franklin and a member of the distinguished Bache family, which numbered so many eminent

[1] *Am. J. Sci.*, 6, *1822.*
[2] *Ibid*, 7, *1823.*
[3] *Ibid*, 6, *1822.*

men of science. He afterwards became professor of chemistry at the Franklin Institute, and in 1841 at the Jefferson Medical College, which chair he held until his death in 1864. He is remembered also as the author of "A System of Chemistry for the Use of Students of Medicine," (Philadelphia, 1819), and of other chemical treatises.

The constitution adopted by the founders of the society, besides the usual provisions for regulating business, contained some unusual features; the officers included an orator, and Article VII prescribed: "An oration on some chemical subject within two months after the commencement of the medical lectures in the University of Pennsylvania, in each year." Since the "Memoirs" published by the society contain no "oration," it is to be feared that the incumbent's efforts were not satisfactory.

Two articles in the constitution deal with fines; "Every member shall be fined $12\frac{1}{2}$ cents for absence each roll, unless satisfactory reasons be offered;" and again: "Any member being elected to office and refusing to serve, shall be fined one dollar."

Another notable provision is as follows: "The society shall appoint, once in each month, some member to read an original chemical essay, for neglect of which, the member so appointed shall be fined one dollar." These fines, with the annual fee of two dollars, were evidently expected to maintain a full treasury.

To become a member of the society, special qualifications were prescribed; after being proposed and seconded, the candidate "shall read an original essay on some chemical subject, on which any member may speak not more than ten minutes." After this trial of his ability, a two-thirds vote of the members present at a subsequent meeting were required to secure election.

It seems to have been easier to be put out of the society than it was to get in, for "any member behaving in a disorderly manner, shall be expelled by consent of two-thirds of the members present."

This mandatory "shall" is used throughout the regulations; the president "shall preserve order," the secretary "shall keep fair minutes," the constitution "shall be revised annually," and so on. To insure against members withdrawing early from

a dull meeting, the "Secretary shall call the roll at the opening and close of each meeting and mark down absentees," each of whom is then fined 12½ cents as stated. Never did a society undertake to control its members with more stringent rules!

The members who subscribed to these regulations were divided into two classes, "Junior" and "Honorary" members, the former corresponding to a class which would now be styled 'Associates," and the latter including both American and foreign chemists of distinction. The junior members numbered thirteen, the honorary members numbered sixty-nine, thirty-one of whom were Europeans. The home list included most of those chemists then living in America, whose labors contributed largely to the foundations of the science in the New World. Brief notices of some of the members will serve to summarize the status of chemistry in the United States for the years 1811–1813.

Dr. Benjamin Smith Barton (1766–1815), held the chair of medicine, natural history, and botany in the University of Pennsylvania. Dr. Barton has been called by his admirers, "the father of American natural history," though there are other claimants for this honorable designation, Mitchill, of New York, and Thomas Jefferson. Dr. Brown Goode, writing of Barton, says he, of all the early Philadelphia naturalists, "had the most salutary influence on the progress of science." He was a leader in the American Philosophical Society, and an agreeable writer on natural history topics, and though he made no contributions to chemistry, was a worthy member of the society.

Dr. Archibald Bruce (1777–1818), one of the pioneers of mineralogical science in America; he had established the American Mineralogical Journal, one year before the date of which I write. His analyses of minerals mark him as a skilful chemist. He held the chair of mineralogy in Columbia College, New York.

Joseph Cloud (1770–1845) was assay master of the United States Mint in Philadelphia, and already distinguished by his researches on palladium (1807).

Thomas Cooper (1759–1840), born in London, had come to America in 1792, with his friend Priestley, whose radical views in politics and religion he shared. Dr. Cooper wrote much on political, ethical, and philosophical subjects, and published some

essays on chemistry. In 1811–14, the period of the Columbian Chemical Society, he held the chair of chemistry at Dickinson College, Carlisle, Pa., and in 1819–34 he held the same position at the College in Columbia, S. C., of which he afterwards became president.

Dr. John Redman Coxe was professor in the medical department of the University of Pennsylvania, having succeeded Dr. Woodhouse. He made several original observations in chemistry published in current periodicals.

Dr. Edward Cutbush (1772–1843) was surgeon of the United States Navy and professor of chemistry in the medical school of the Columbian University, Washington (1825–27). He has another honorable claim to distinction, having been the founder in 1819 of the Columbian Institute for the Promotion of Arts and Sciences in Washington, a sort of precursor of the Smithsonian Institution.

Passing with brief mention Dr. Elisha de Butts, professor of chemistry in the College of Maryland, Prof. Benjamin de Witt, of New York, and Dr. John Syng Dorsey, already mentioned as a member of the society founded in 1792, we reach the more familiar name of Dr. John Griscom, "the acknowledged head of all teachers of chemistry in New York City," for more than thirty years.

The next name in the alphabetical list of members is that of Robert Hare, professor of natural philosophy in the University of Pennsylvania, whose career we have already noticed.

Dr. David Hosack (1769–1835), professor of botany and materia medica in Columbia College, New York, is best known as the founder of the first public botanic garden in the United States, in 1801. His contributions to science were chiefly in medicine. The tragic circumstances of his death have been nearly forgotten; he died of shock at the disastrous conflagration in New York City in 1835, which swept away his property to the value of $300,000.

Dr. Henry Jackson, professor of chemistry at Athens College, Georgia, is followed by His Excellency, James Madison, LL.D., President of the United States of America, whose name added luster to the rolls of the society, but whose claim to the membership can only be based on extensive general information.

Dr. John Manners, of Philadelphia, affixes to his name the initials F.A.N.S., the Academy of Natural Sciences, having been founded one year before the printing of the list of members. His contributions to the Chemical Society will be noted below.

Dr. John Maclean, (1771–1840), was the first professor of chemistry in the College of New Jersey, now Princeton University, to which chair he was elected in 1797. In accordance with the prevailing custom, he also gave the instruction in astronomy, mathematics, natural philosophy, and natural history; this fact is ample apology for his not appearing in the ranks of original investigators. Prof. Maclean published in 1797, "Two Lectures on Combustion," in which he upheld the views of Lavoisier, as opposed to the phlogistic theory maintained by Dr. Priestley.

The Hon. Samuel L. Mitchill, M.D., F.R.S.E. (1764–1831), professor of chemistry and natural history in Columbia College from 1792, was active in many branches of scientific research. In 1798 he established the New York Medical Repository, which for sixteen years was an influential organ in recording and diffusing progress in general science, as well as in medicine. His zeal for science did not prevent his taking part in national affairs, for he occupied a seat in the senate of the United States from 1804.

Dr. Thomas D. Mitchell, F.A.N.S., was one of the most active members of the society, frequently contributing to its memoirs.

Passing by Dr. John C. Osborne, professor of the institutes and practice of medicine in Columbia College, New York; Dr. Joseph Parish, of Philadelphia; Mr. Robert Patterson (1743–1824), professor of mathematics and lecturer on natural philosophy in the University of Pennsylvania, director of the United States Mint, and afterwards (1819) president of the American Philosophical Society; Dr. Nathaniel Potter, professor of the theory and practice of medicine, University of Maryland, we reach the eminent Dr. Benjamin Rush, professor of the institutes and practice of medicine in the University of Pennsylvania. Dr. Rush (1745–1813) has been characterized by Benjamin Silliman as "undoubtedly the first Professor of Chemistry in America," his appointment dating August 1, 1769. In his

busy life, besides his professorial chair, he filled the positions of surgeon-general of the United States Army (1777), treasurer of the Mint, president of the Society for the Abolition of Slavery, vice-president of the Bible Society of Philadelphia, and conducted a large medical practice in the same city.

Dr. Adam Seybert (d. 1825), was one of the earliest American chemists to make a series of analyses of the air by eudiometric methods. Having made twenty-seven air analyses during a voyage across the Atlantic, he compared the results with others made on land and drew the conclusion that the sea exerted purifying power over the air; his paper before the American Philosophical Society bore the date 1797.

Benjamin Silliman is a name so familiar to American chemists as to require no eulogium in this place. At the founding of the chemical society he was forty years of age and had held the chair of chemistry in Yale College for ten years. It should be remembered that he did not begin publishing the American Journal of Science until 1818.

Dr. John S. Stringham, professor of chemistry in New York, (institution not specified); Dr. Jared Troust, (whose name should be written Gerard Troost), lecturer on mineralogy in the Academy of Natural Sciences, Philadelphia, and afterwards professor of chemistry, mineralogy, and geology in Nashville University (1828–50); Lawrence Washington, Esq., of Virginia, and Dr. Caspar Wistar, professor of anatomy in the University of Pennsylvania, with his relative Charles Wistar, complete the roll of home members.

The prominence of medical men on this list is evident, and is easily explained. Before the days of schools of science, and before colleges devoted a portion of their curricula to scientific studies, almost the only training in science received by American youth was in the medical schools. The chairs of natural history and of the physical sciences were almost exclusively held by physicians whose education more nearly qualified them for teaching these branches of knowledge than the graduates of the classical courses customary in all colleges.

To elevate the standard of membership in the Columbian Chemical Society, a number of distinguished foreigners were enrolled. France contributed Adet, Berthollet, Chaptal, Dey-

eux, Abbé Hauy, Bouillon-Lagrange, Gay-Lussac, Monge, Guyton de Morveau, Parmentier, Pelletier, Sequin, Thénard and Vauquelin. Great Britain was represented by Sir Joseph Banks, John Dalton, Sir Humphry Davy, John Davy, J. A. de Luc, Hatchett, Dr. William Henry, Sir William Herschel, Dr. John Hope, John Murray, William Nicholson, Dr. G. Pearson, Mr. W. H. Pepys, Dr. Thomas Thomson, Alexander Tilloch and Dr. William Hyde Wollaston. Spain was represented by Professor Proust of Madrid, and the other countries of Europe had not a single representative. The absence of such eminent names as Richter, Klaproth, Stromeyer, Trommsdorff and Gehlen, of Germany, as well as of Berzelius, the Swede, presumably indicates that at this early date, communication and exchange of courtesies with Germany and Northern Europe was less common than with England and France.

The Columbian Chemical Society of Philadelphia published in 1813 one volume of Memoirs;[1] this forms a book of 221 pages, octavo, and bears the imprint of Isaac Peirce, No. 3 South Fourth Street, Philadelphia. It contains twenty-six essays, by ten writers, on a great variety of topics, original, speculative and practical.

No less than eight of the papers are from the pen of Dr. Thomas D. Mitchell, and these I proceed to review. Dr. Mitchell's "Remarks on the Phlogistic and Antiphlogistic Systems of Chemistry" opens the volume; in this essay he supports the Lavoisierian theory of combustion, stating that there is "no necessity for the principle of inflammability;" he cites the experiment of Woodhouse, who obtained an inflammable air by heating charcoal with scales of iron, both being free from water, and points out that Cruikshank, of Woolwich, demonstrated that the inflammable gas thus obtained is gaseous oxide of carbon (carbon monoxide), discovered by Priestley in 1799, and combustible, although containing no hydrogen. He compares combustion with neutralization of an acid and base, saying: "Inflammation and acidity are effects resulting from the action of relative causes, and not attributable to a single agent or principle."

Dr. Mitchell's second paper, "Remarks on Heat," deals with

[1] Copies of the Memoirs are found in Philadelphia libraries, and in the private library of the writer.

speculations on latent heat, objecting to this term and to Dr. Black's theories.

In a paper entitled "On Muriatic and Oxy-Muriatic Acids," Dr. Mitchell vehemently attacks the views of Sir Humphry Davy as to the non-existence of oxygen in muriatic acid, clinging to the statement of Lavoisier, that all acids contain oxygen. In a section on combustion, he remarks, "we have incontestible proof that oxygen gas contains light," and he regards combustion as accompanied by the decomposition of oxygen gas.

Dr. Mitchell's fourth paper is of a more practical character, being the "Analysis of Malachite" from Perkioming, Pennsylvania. The result is given as follows: "120 grains of the green carbonate contained carbonic acid, 30 grains; quartz and silicious earth, 68 grains; brown oxide of copper, 15 grains; loss in the process, 7 grains."

The specimen was evidently a poor one; no account was taken of the water, and reporting results in percentages was not in vogue.

In some "Remarks on Putrefaction," the same writer discusses the action of antiseptics, and attributes the virtue of nitrate of potash to the increase of cold produced by the muriate of soda.

Dr. Mitchell's "Chemical View of Secretion," and his "Analysis of Professor Coxe's Essay on Combustion and Acidification," are polemical and speculative; in his "Remarks on the Atmosphere" he argues to prove the atmosphere a chemical union of oxygen and nitrogen.

Franklin Bache contributes three essays to the volume. "An Inquiry into What Circumstances Will Warrant us Justly to Reckon any Substance a Principle of a Common Property of Any Set of Bodies," discusses the much disputed question of that day, whether hydrogen as well as oxygen can be an acid-forming principle. His conclusion being, "it may." Bache's second paper is entitled, "An Inquiry Whether Mr. Berthollet was Warranted from Certain Experiments in Framing the Law of Chemical Affinity, that it is Directly Proportional to the Quantity of Matter." In this essay the author points out "the probable way in which this great philosopher fell into this great error." In a third paper styled "Thoughts on the Expediency of

Changing Parts of the Chemical Nomenclature," Mr. Bache proposes the following names: Nitral acid forming nitrotes, nitril acid forming nitrutes, nitrous forming nitrites, and nitric acid forming nitrates, for the several acid-forming oxides of nitrogen. Fortunately his influence was insufficient to inflict these names on chemical language.

Dr. John Manners contributed four papers to the Memoirs. (1) "Experiments and Observations on the Effect of Light on Vegetables and upon the Physiology of Leaves," which abounds in quotations from Darwin's "Botanic Garden." (2) "Analysis of a Mineral Spring at the Willow Grove," (fourteen miles from Philadelphia). In this the author was assisted by Dr. Mitchell. They report the action of each testing solution on the water, and conclude that the water contains iron and sulphuretted hydrogen, and show the absence of lime, copper and carbonic acid." (3) "On the Production of Sulphuretted Hydrogen by the Action of Black Sulphuric Acid, Diluted with Water on Iron Nails." The acid had been blackened by a piece of cork which had fallen in. (4) "Experiments and Observations on Putrefaction." In this paper Dr. Manners tested the influence of carbonic acid, hydrogen and other gases on putrefying flesh, and also attempted to collect and analyze the gases generated by the same. He concludes that "putrefaction depends on a destruction of the equilibrium of attractions which exists in the elementary principles of which the animal substance is composed in a healthy state, occasioned by the loss of vitality in consequence of which new compositions and decompositions ensue."

Professor Cutbush, President of the Society, wrote "On the Prognostic Signs of the Weather," and "On the Oxyacetite of Iron as a Test for the Discovery of Arsenic;" the latter being a good presentation of his discovery, subsequently used as a quantitative method by Kotschoubey.

Mr. Samuel F. Carl, one of the junior members, has two papers containing analyses, the first of the mineral spring at Bordentown, New Jersey, which proved to be a "carbonated chalybeate water," and the second of two specimens referred to him by the society; these proved to be respectively an iron ore

and a ferruginous copper ore. The method of reporting results seems very crude to a modern analytical chemist.

Dr. Joel B. Sutherland contributes "Speculations on Lime," in which he claims that if mortar be made with sand containing common salt, the resultant compound gives so much coldness to the mass that during the whole summer vapor is almost incessantly precipitated on the wall with which it is plastered. He also wrote "A Few Remarks on the Nature of the Nervous Influence." Akin to the latter are the "Thoughts on the Principle of Excitability," by George Ferdinand Lehman, who also wrote "On the Emission of Oxygen by Plants."

Mr. William Hembel, Jr., has two papers, one entitled "Observations on the Formation of Muriate of Potash in the Process of Preparing the Hyperoxymuriate of Potash," which is complicated by the belief that hydrochloric acid is an oxygen compound; and another entitled "A New Method of Mounting Woulfe's Apparatus," which is unintelligible owing to the omission of a woodcut to which the text refers.

Mr. Edward Brux, of France, one of the junior members, writes "Upon the Effects of Various Gases upon the Living Animal Body," which consists largely of speculations: notwithstanding which he cites an admirable passage from Dr. Bostock; "Physiologists have, in general, been more inclined to form hypotheses than to execute experiments, and it has necessarily ensued from this unfortunate propensity that their science has advanced more slowly than perhaps any other department of natural philosophy." Unfortunately this truth was not fully recognized by the members of the Columbian Chemical Society.

A contemporary journal (N. Y. Medical Repository), in reviewing the "Memoirs," uses the following quaint language: "It is highly gratifying to behold a band of worthies like those before us, laboring to analyze the compounds which they find ready made, to form by synthesis new combinations in the laboratory, and thereby to deduce correct doctrines from the facts which are disclosed. We cordially congratulate them on their noble occupation and on the progress they have made. We hope they will be persevering and undaunted. And if from this beginning there shall arise great improvements in theoretical disquisition, as well as in economical exercise, we shall rejoice

with a mingled glow of amicable and patriotic sentiment."

III. THE DELAWARE CHEMICAL AND GEOLOGICAL SOCIETY.

The Delaware Chemical and Geological Society was organized at Delhi, Delaware County, New York, September 6, 1821; the first meeting was held at the hotel of G. H. Edgerton in the village, and the following officers were chosen:

President—Charles A. Foote.
Vice-President—Rev. James P. F. Clark.
Recording Secretary—Charles Hathaway.
Corresponding Secretary—Dr. Calvin Howard.
Treasurer—Selah R. Hobbie.
Directors—Cornelius R. Fitch, R. W. Stockton, Ebenezer Steele.

The society was composed of "between forty and fifty well-informed and respectable inhabitants" of the County of Delaware. The following gentlemen were elected corresponding members: Colonel Henry Leavenworth, U. S. A.; Edwin Croswell, of Catskill, and O. Rice, of Troy.

The society had for its object the improvement of the members in literature and science, especially in chemistry and mineralogy. The members planned to form a library and to secure a chemical laboratory; they made a collection of the minerals and rocks of the region, which was still preserved in the Delaware Academy in 1856. The meetings of the society were held quarterly, and at each an essay or an "original scientific discourse" was presented; it was, however, not long sustained.

In reviewing the condition of chemical science in the United States, as indicated by the membership and achievements of these early societies, we note that those who held the most prominent places were handicapped by the necessity of devoting a large part of their intellectual energy to topics quite outside of the domain of chemistry itself. The active members were either busy with the art of healing, or with teaching several branches of the physical and natural sciences, and too often chemistry was regarded in the colleges as a kind of side issue, or appendix to the more important subjects of instruction. This was caused

by the necessity of earning a competence at a time when there was no opportunity of reaping pecuniary rewards by skill as an analyst, or by the application of science to the manufacture of products involving chemical knowledge. Indeed, in default of this stimulus to laboratory work, it is not surprising that the papers read to the societies were largely either reviews of the grand discoveries made by Europeans, or essays in which the imaginative faculty was given free play, it being far easier to indulge in speculation than to discover new facts.

In the early struggles of a country to secure a place among nations, few men of ability can devote their energies to the pursuit of science for science's sake; the environment is more favorable to development of the inventive faculty than of the peculiar talent for conducting abstruse researches in an exact science. Add to this the limited facilities for acquiring chemical knowledge in the New World, and the distance of amateurs from the European head-centers of learning, and it is certainly noteworthy that American chemists combined to form associations for mutual improvement and the advancement of their calling at so early a period.

A fourth attempt to establish a chemical society was made at New York City in 1876; the organization was at first somewhat restricted in its plan, but in 1892 a change in its constitution was effected, which broadened its scope, and it now forms a strong, influential and truly national society. Its 1106 members, working in nine chartered sections, represent forty-seven states and territories, besides several countries of Europe, South America, and distant Australia. Its Journal, comprising 1150 pages annually, is an authoritative medium for the preservation and diffusion of the researches made in the United States, and its annual meetings, held in diverse localities, strengthen the bonds which unite its members in good fellowship, and in the pursuit of their common profession. *Long may the American Chemical Society continue in its prosperous career!*

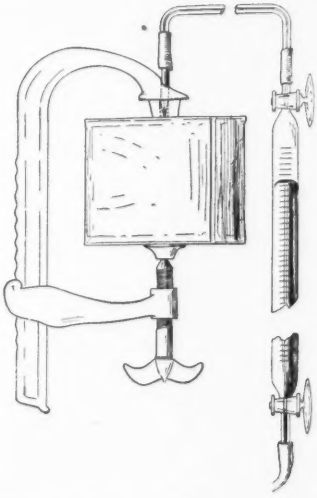
METHOD OF COLLECTING AND ANALYZING THE GASES IN CANNED GOODS.[1]

By Charles A. Doremus.

(Second paper.)

Received July 12, 1897.

THE first paper on this subject was read at the Second International Congress of Applied Chemistry, held last summer in Paris. As the publication of the proceedings has been delayed and would not reach some to whom this topic may be of interest, additional tests and analyses have been made and the accompanying illustration will possibly induce others to experiment further.



The first analyses of the gases in canned goods were effected in a Wilkinson gas analysis eudiometer. This instrument is similar in form to a Lunge's nitrometer. The graduated tube has a glass stop-cock at its upper extremity, above which is a detachable funnel. A large inverted funnel was joined to the lower end of this instrument, and the whole filled with water in a pneumatic trough. The can was punctured beneath the funnel.

[1] Read before the New York Section, June 11, 1897.

The bubbles of gas rose through the water and were measured and analyzed.

This operation was inconvenient. It permitted the gases to come into contact with much water in which some portion of gas might readily dissolve.

These inconveniences are overcome by the aid of the following device. A beveled, hollow, steel needle is attached to the upper arm of an adjustable clamp. The point and lower part of the shaft are covered by a rubber stopper, which serves as a soft pad; the lower arm is moved along the body of the clamp until the can to be pierced is held between the rubber stopper and the head of the screw. The upper part of the needle is connected by means of a capillary tube filled either with water or mercury, with a receiver also filled with either of these liquids. The receiver may be either a stop-cock eudiometer as just described, or a eudiometer with leveling tube attached.

The apparatus adjusted, a turn or two of the screw clamps the can tightly between the rubber pad at the top and the screw head below. The rubber yields to the pressure, making a tight joint around the needle. When the latter pierces the tin the contained gases of the can escape gently into the eudiometer.

Cans containing sound goods present a collapsed condition, owing to the condensation of the steam after processing. "Rattlers" are cans which yield to pressure. "Swells" are cans which seem ready to burst. Enough gas can generally be obtained from either of the above for systematic analysis. Sixty to eighty cc. of gas can often be collected. The internal pressure is sometimes sufficient to split a seam and allow some of the contents to escape, or to burst a can with violence.

After collecting the gases the can should be opened and its contents carefully examined. A putrid odor indicates, of course, decomposition. Where this is absent and the food appears perfectly sound and undecomposed the distention may be due to different causes.

A bacteriological examination is advisable.[1] Through the kindness of Dr. Lederle, of the Board of Health, samples of various canned goods have been sent me and submitted to analysis.

[1] Putrefaction of Albumins, O. Emmerling: *Ber. d. chem. Ges.*, 29, 2721–2726.

Carbon dioxide forms the chief constituent of the gaseous mixture where putrid odor abounds. In other cases hydrogen predominates. The contents of the cans show little change. There is no offensive odor. There is absence of bacteria. There are positive indications of the corrosion of the inner metallic surfaces. Sometimes there is a discoloration of the can as if a slight amount of hydrogen sulphide had been formed. The contents of such cans also yield the reactions of the metals. Hydrogen has also been found where the evidences of corrosion were not marked. With the above clues afforded by the inspection of the contents of the can, the gases in the eudiometer may be subjected to the action of proper reagents in such order as to determine at least the main constituents. The reagents may be allowed to enter the stop-cock eudiometer, or the gases be transferred to pipettes as is customary in gas analysis. The recognition of traces of substances whose odor is very marked is difficult; for some we have no adequate tests.

COLLEGE OF THE CITY OF NEW YORK.

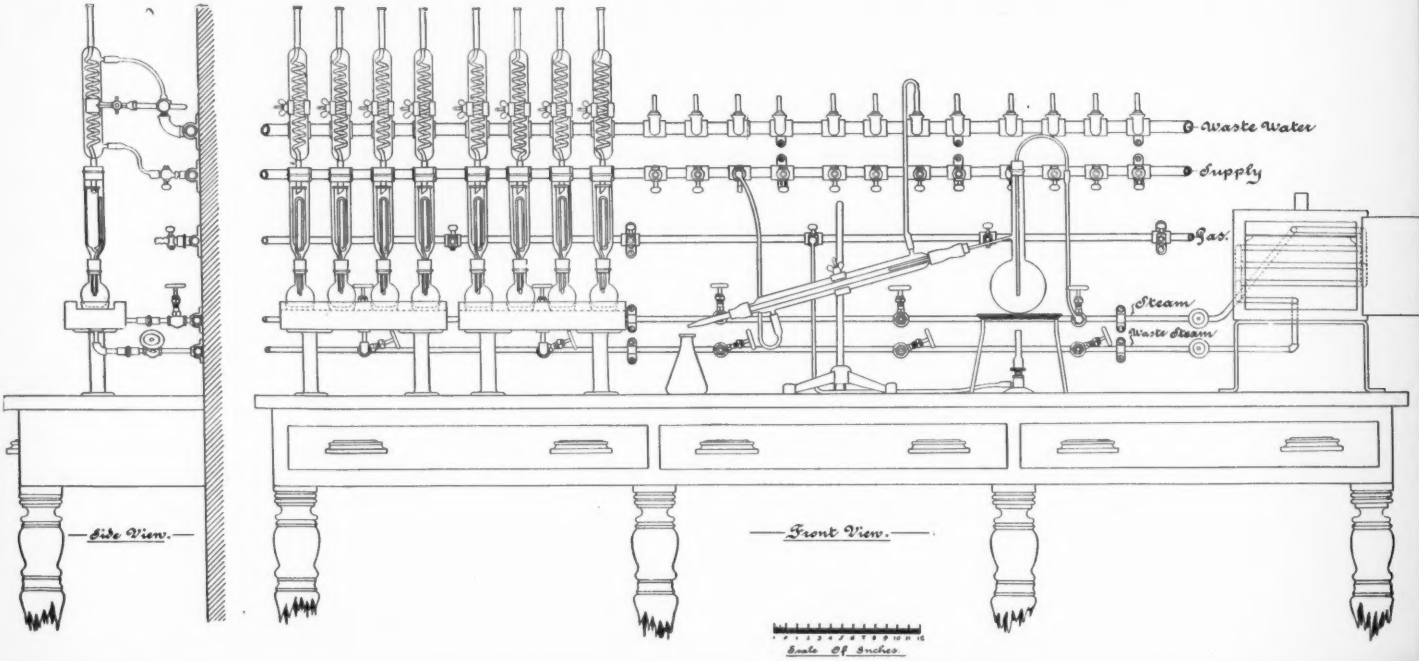
MECHANICAL ARRANGEMENT OF FAT EXTRACTION APPARATUS.

BY G. J. VOLCKENING.

Received July 17, 1897.

THE apparatus shown in the accompanying drawing has been in use in the Chemical Laboratory of the Brooklyn Health Department for the past eighteen months. It was designed to meet the demand often experienced in food laboratories where large numbers of samples of milk are submitted for analysis. Too often is the chemist given an unoccupied room of no apparent use for other purposes and is told to build a laboratory. The disadvantage of a small laboratory was experienced. A separate room could not be given up for fat extraction; consequently this work had to be performed in the general and only room in the presence of naked flames. It was, therefore, necessary to produce a piece of apparatus that was compact, free from any chance of explosion, of a capacity sufficient to meet all demands and simple enough to be operated by the laboratory boy. About two feet above the table, on the wall, is

Mechanical Arrangement Of Fat Extraction Apparatus.



fastened the waste pipe, which receives the water after it has passed through the condensers. In order to obviate any back pressure the pipe is made larger and carried direct to the sewer, without receiving the discharge from any other fixture. The inlet tubes are built up by using a T, an elbow, reducer, and short brass pipe about three inches long. The condensers are supported by clamps to these inlet tubes. The overflows from the condensers are connected by means of rubber tubing to the inlet tubes, which serve a double purpose; that of posts supporting the apparatus, and at the same time acting as outlets for the waste water.

The cold water supply pipe is securely fastened to the wall about six inches below and parallel to the line of waste. As the building was not supplied with a tank, the pressure in the general house supply often dropped below ten pounds. It was found necessary, in order to maintain a constant supply of water at all times, to run a separate line of pipe from the street direct to this table without being connected to any other fixture. There are twenty outlets on the table, each being provided with a separate stop-cock directly under the inlet tube of the waste; consequently each condenser can be operated independently of the others. Thus the number used at any time will depend upon the amount of work on hand.

The ether is heated on gun-metal steam tables, which have been tested up to a pressure of fifty pounds per sqnare inch. In order to give closer contact and thus reduce the time of the operation, small capsules are placed on the table and partly filled with water. The bottoms of the flasks coming in contact with the hot water shortens the time of vaporizing the ether. As a substitute for the capsules a piece of thin felt moistened with water will answer the same purpose. Each steam table will support four sets of extractors. It will be seen by referring to the drawing that each table can be operated independently by means of the separate stop-cocks, and further, if only one table is required the others can be removed with their accompanying apparatus, thus allowing the space to be occupied for other purposes. The steam is generated by an upright tubular boiler heated by gas.

The whole or part of the laboratory table can be used for

other operations by disconnecting the apparatus. The drawing shows the table as it is used during the winter months, three steam tables being removed and in their place apparatus set up for steam distillation.

THE COMPOSITION OF HUMUS.

By Harry Snyder.

Received July 6, 1897.

THE organic compounds of the soil to which the term humus is collectively applied, are a group about which but little is actually known. The humus compounds have not been extensively studied because of the difficulty of separating and obtaining them in a pure state. They do not form well-defined crystalline compounds, and they are all about equally soluble in various reagents. In fact, the analyst, when working with the humus compounds, is never sure whether he is working with a single compound or a mixture of several compounds.

The usual method employed in soil analysis for the determination of the humus compounds is the Grandeau or some modification of that method, which consists of first treating the soil with cold dilute hydrochloric acid to remove the lime, and then, after washing with distilled water, extracting the humus materials with a dilute ammonia solution. The humus extract is evaporated to dryness, dried, weighed, ignited, weighed again, and the loss of weight calculated as humus.

Inasmuch as the organic compounds of the soil may be derived from so many different sources, as any form of decayed animal or vegetable matter, it must necessarily follow that humus is very complex in composition. It seemed best, in this study of the composition of humus, to produce the humus from known materials, rather than to start with humus from unknown sources. Humus was prepared in the following way: A soil containing only a small known amount of organic material was used. About 200 grams of sugar were mixed with 3,000 grams of soil, placed in a tight box, and allowed to undergo humus formation, out of doors, for one year. Humus was produced in this way from a variety of materials, as cow manure, green clover, meat scraps, wheat flour, saw dust, oat straw, and sugar.

The humus materials produced from these various substances were obtained by extracting the soil, after treatment with dilute hydrochloric acid and distilled water, with a three per cent. potassium hydroxide solution. The alkaline humus extracts were neutralized with hydrochloric acid, which gave black and brown precipitates of humus materials, which were washed, dried, and prepared for analysis. The precipitated humus materials contained from five to twelve per cent. of ash, and had the following ultimate compositions, on an ash-free basis:

	Humus Produced by						
	Cow manure. Per cent.	Green clover. Per cent.	Meat scraps. Per cent.	Wheat flour. Per cent.	Oat straw. Per cent.	Sawdust. Per cent.	Sugar. Per cent.
Carbon.....	41.95	54.22	48.77	51.02	54.30	49.28	57.84
Hydrogen...	6.26	3.40	4.30	3.82	2.48	3.33	3.04
Nitrogen....	6.16	8.24	10.96	5.02	2.50	0.32	0.08
Oxygen	45.65	34.14	35.97	40.14	40.72	47.07	39.04
Total.....	100.00	100.00	100.00	100.00	100.00	100.00	100.00

	Highest. Per cent.	Lowest. Per cent.	Difference. Per cent.
Carbon.....	57.84 sugar.	41.95 cow manure.	15.89
Hydrogen ...	6.26 cow manure.	2.48 oat straw.	3.78
Nitrogen	10.96 meat scraps.	0.08 sugar.	10.88
Oxygen	47.07 sawdust.	34.14 green clover.	12.93

The differences in composition are noticeable. The humus produced by each material, as meat scraps, green clover, or sawdust, is different from the humus produced by every other material. There is not a general similarity in composition between the humus produced by any two of the materials. The humus produced by sugar may be taken as a type of a non-nitrogenous humus. The small amount of nitrogen present in the sugar humus has been derived from the nitrogen present in the soil. The humus from meat scraps may be taken as a type of humus produced from a nitrogenous material. The nitrogen content of the humus ranges from about one-tenth per cent. in sugar humus to nearly eleven per cent. in the meat scraps humus. The humus from materials as meat scraps and green clover must be exceedingly complex, because each material is composed of both nitrogenous and non-nitrogenous compounds, and each class of compounds is capable of being

split up into still other compounds, each one having a different action in humification processes. It is evident that any formulas applied to the compounds, as a whole, would, to say the least, fail to express the composition of humus.

Although the proximate composition of humus as yet, can not be given, or formulas assigned to these compounds, the nature of the humus as nitrogenous or non-nitrogenous can be determined.

There appears to have been no classification of the humus compounds proposed since the classification of Mülder, in 1840, as follows:

	Ulmin and ulmic acid. Per cent.	Humin and humic acid. Per cent.	Crenic acid. Per cent.	Approcrenic acid. Per cent.
Carbon	67.1	64.4	44.0	34.4
Hydrogen	4.2	4.3	5.5	3.5
Nitrogen	...	...	3.9	3.0
Oxygen	28.7	31.3	46.6	39.1
	100.00	100.00	100.00	100.00

Corresponding to $C_{40}H_{28}O_{12} + H_2O$; $C_{21}H_{24}O_{12} + 3H_2O$; $C_{12}H_{12}O_8$ (?); $C_{24}H_{24}O_{12}$ (?).

None of the humus materials produced in these culture experiments have the same composition as given above. The sawdust and sugar humus approach in composition nearest to the humic and ulmic compounds. The differences are, however, great.

It would seem best, in the present state of knowledge, to make the divisions on the basis of nitrogen, as:

I. The non-nitrogenous humus group, as sugar humus.

II. The nitrogenous group, divided into three or four subgroups, as (1) humus containing one to two per cent. nitrogen, as sawdust humus; (2) humus containing two to four per cent. nitrogen, as oat straw humus; (3) humus containing four to eight per cent. nitrogen, as cow manure and clover humus; and (4) humus containing over eight or nine per cent. nitrogen, as meat scrap humus.

Such a division would give an approximate idea as to the nature of the materials from which the humus has been derived, as well as an approximate idea of its agricultural value. As ordinarily used, the term humus is a very indefinite one so far

as conveying any idea as to its chemical composition or probable value.

Formation of Humates.—The analysis of the ash from the precipitated humus compounds shows the presence of potassium, calcium, iron, aluminum, phosphorus, sulphur, and other elements. There is every indication that these elements are in organic combination with the carbon, hydrogen, nitrogen, and oxygen of the humus. When the alkaline humus solution is neutralized, the ash elements are precipitated with the humus materials. The mineral matter combined with the humus is different in composition and solubility from ordinary soil. The average composition of the ash from eight samples of precipitated humus was found to be as follows:

	Per cent.
Insoluble matter (HCl)	61.97
Potash	7.50
Soda	8.13
Lime	0.09
Magnesia	0.36
Alumina	3.48
Ferric oxide	3.12
Phosphorus pentoxide	12.37
Sulphur trioxide	0.98
Carbon dioxide	1.64

Is the mineral matter, combined with humus, derived entirely from the mineral matter originally present in the humus-forming material, or is a part of it derived from the soil by the chemical action of the humus? That is, does the humus combine with the mineral matter of the soil to form compounds known as humates? In order to obtain data upon this question, initial and final weights of the soil and humus-forming materials used in the humus production experiments reported, were made, and the total grams of humic phosphoric acid and potash, in both the original soil and humus material, as well as the final product of the humus, were calculated. In many cases there were decided gains, showing that some of the mineral matter of the soil had entered into chemical combination with the humus-forming materials. In the following table the figures given for the original soil and humus are for the amounts present in the soil in humic forms plus the total amount of mineral matter in the substance used:

	Humic phosphorus pentoxide. Grams.	Humic potash. Grams.
Cow manure humus.		
Original soil and manure	1.17	1.06
Final humus product	1.62	1.27
Green clover humus.		
Original soil and clover	3.21	5.26
Final humus product	3.74	4.93
Meat scraps humus.		
Original soil and meat scraps	1.07	0.25
Final humus product	1.18	0.36
Sawdust humus.		
Original soil and sawdust	0.85	0.67
Final humus product	0.78	0.70
Flour humus.		
Original soil and flour	0.60	0.32
Final humus product	0.71	0.48
Oat straw humus.		
Original soil and straw	1.02	2.42
Final humus product	1.03	2.41

There appears to be a great difference in the power which various materials possess of entering into chemical combination with the mineral matter of the soil to form humates. Some of the nitrogenous compounds seem to have a greater power of combining than the non-nitrogenous compounds. There is also a great difference in soils: some combine with the humus materials more readily than others.

The ultimate composition of the humus from different types of soil shows as wide a range as in the case of the humus prepared from the culture experiments. The nitrogen content of the humus ranges from one to ten per cent. The following examples show a range from six to ten. No. 1 is a sample made up of equal parts of eight rich prairie soils. No. 2 is a soil that has been under cultivation for a number of years. Nos. 3 and 4 are different types of soil. No. 3 has never been under cultivation, while No. 4 is a similar soil which has been cultivated for about forty years to small grains.

	No. 1. Per cent.	No. 2. Per cent.	No. 3. Per cent	No. 4. Per cent.
Carbon	45.12	48.16	44.12	50.10
Hydrogen	3.67	5.40	6.00	4.80
Nitrogen	10.37	9.12	8.12	6.54
Oxygen	28.60	33.16	35.16	33.66
Ash	12.24	4.16	6.60	4.90

The humus from soils Nos. 1 and 2 would belong to the fourth class, while Nos. 3 and 4 would belong to the third class of nitrogenous humus compounds. For reasons given it would be impossible to assign, from these analyses, any formulas to the humus. The next best thing that can be done is to assign to the humus its probable agricultural value, which can best be done on the basis of the nitrogen content of the humus. This would involve simply a determination of the humus, and also a determination of the nitrogen content of the humus. The following working directions for these two determinations have been found to work well with ordinary soils.

Determination of Humus.—Weigh out either five or ten grams of soil into a 200 cc. wide mouthed glass-stoppered bottle. If the soil is poor in organic matter, fifteen or twenty grams should be taken. Add 100 cc. of a one per cent. solution of hydrochloric acid. If the soil contains more than one per cent. lime, then a two per cent. solution of hydrochloric acid may be used. Place the stopper in the bottle and shake vigorously. After allowing the acid to act on the soil for five or ten hours the solution is decanted into a filter, a fresh quantity of 100 cc. of acid is added, it is decanted, and the contents of the bottle are transferred to the funnel. The soil, in the funnel, is then washed with the dilute acid until no reaction for lime is obtained, and then with distilled water until the washings are only slightly turbid with silver nitrate. After receiving the above treatment the soil is transferred from the funnel to the stoppered bottle, using 150 cc. of a three per cent. solution of ammonia. The bottle containing the soil and ammonia solution is occasionally shaken, and after five or six hours the solution is decanted into a 500 cc. measuring flask. A fresh quantity of about 100 cc. of ammonia is added to the soil in the bottle, and after acting on the soil for three or four hours it is decanted and added to the first extract. After the third extraction, the extract usually becomes nearly colorless. After the fourth extraction the humus solution in the flask is made up to 500 cc. and allowed to settle. If the soil contains a large amount of fine clay it will be necessary to allow from two to ten hours, or longer, for the soil particles to settle. A 50 or 100 cc. portion of the filtered humus extract is evaporated to dryness in a tared platinum dish. After

drying in an air-bath at 101° or 102° (on account of the tenacity with which the humus retains water), the dish with the humus materials is weighed, then ignited, and weighed again. The loss of weight is calculated as humus. The humus extract may be either black or brown.

Nitrogen Content of the Humus.—Either five or ten grams of soil are first treated with dilute hydrochloric acid, in the same way as in the humus determination. If the soil contains only a small amount of organic material, fifteen or twenty grams should be taken for this determination. After treatment with acid the soil is extracted with a three per cent. solution of sodium hydroxide in the same way as for the ammonia extraction. Two hundred cc. of the filtered solution are evaporated nearly to dryness in a Kjeldahl distillation flask, after first making the solution acid with sulphuric acid. The nitrogen determination is then completed in the usual way.

THE ACTION OF CERTAIN BODIES ON THE DIGESTIVE FERMENTS.

By Frank D. Simons.

Received June 29, 1897.

VERY little attention seems to have been given to the study of the action of some of our common coloring matters, flavoring extracts, and preservatives on the digestive ferments. The object of my work, therefore, has been to test, from a physiological standpoint, the deportment of members of the above three classes of bodies towards digestion.

As far as my searches have extended, I have been able to find but very little literature bearing on this subject. Professor Chittenden, of the Sheffield Scientific School, has furnished many valuable contributions to our knowledge of digestion. He includes in a list of bodies antagonistic to the peptic ferment, potassium permanganate, borax, ammonia-alum, sodium salicylate, quinine, and the salts of nearly all of the alkaloids.

Dr. H. A. Weber[1] investigated the behavior of three coal-tar coloring matters (*viz.*, oroline yellow, saffoline, and magenta) towards digestion. Although these bodies have been included in the list of harmless colors, yet he found that each one, even

[1] This Journal, **18**, 1092, *1896*.

when taken in a very minute quantity, arrested digestion, some of them that of the stomach, others that of the intestines, though in no case did he find that any one substance alone had a retarding effect on both peptic and pancreatic digestion. From his results then, it would seem that these substances are very harmful, inasmuch as they interfere seriously with the natural functions of the digestive organs, or more correctly speaking, with their secretions.

As an example of the possible danger from the indiscriminate use of these comparatively unknown (at least so far as concerns their relations toward digestion) colors, we quote the results of Mr. Weber's experiments with oroline yellow on stomachic digestion:

"This color was one of a series employed in the coloring of confectionery, and was found to be what is known in the trade as acid yellow or fast yellow, and is a mixture of sodium amidoazobenzenedisulphonate with sodium amidoazobenzenemonosulphonate.

	Amount of color. Gram.	Amount of fibrin. Gram.	Amount of pepsin. Gram.	Duration of experiment. Hours.	Amount of fibrin dissolved. Gram.
1	0.0	1	0.020	3	1.00
2	1.0	1	0.020	3	0.10
3	0.5	1	0.020	3	0.12
4	0.25	1	0.020	3	0.22
5	0.125	1	0.020	3	0.35
6	0.062	1	0.020	3	0.73

From this it will be seen that even in test No. 6, where the color employed amounted to only one part in 1,600 parts of the solution, the presence of the color had still a depressing effect. On the whole it must be conceded that this color has a marked and injurious effect on peptic digestion."

Now when we see what a small portion of the poison (I call it so, for undoubtedly it is) will retard digestion, the only natural inference, which one might draw, would be that it is antagonistic to the normal action of the organs. However, that is a question for the physician rather than for the chemist, for while the latter performs the experiments, the former applies their results.

In carrying on an artificial process of digestion the substance usually employed to be digested is freshly prepared blood fibrin or purified and coagulated egg-albumin.

To prepare the former the blood fresh from the artery must be well whipped, and the fibrin thus obtained washed quickly and thoroughly with water. When washed well, it should be perfectly white, showing no tint of red. While the freshly prepared fibrin is always better for the tests, yet, as the investigator is seldom in a position where this can be accomplished without some difficulty and loss of time, it may be preserved to good advantage in alcohol; in this manner it can be kept from decomposition for some time. Before using, however, it must be washed entirely free from the spirits, then dried, and the amount of material desired weighed.

To prepare coagulated egg-albumin treat the whites of freshly laid eggs with an equal volume of water, shake well, and exactly neutralize with hydrochloric acid. Then filter until the filtrate is comparatively clear, and pour into about an equal volume of boiling water. Render faintly acid with acetic acid[1] and heat to vigorous boiling. The precipitate is now filtered off, and washed several times with boiling water. It is then ready for use, and like fibrin may be preserved to good advantage in alcohol. When the process has been rightly carried on, the albumin should be perfectly white, firm, and capable of being easily washed and dried. There should be no sticky feeling when held in the hands, and when such is the case, it must be submitted to further boiling, and perhaps even to a slight neutralization.

I found the albumin to be better for my experiments than the fibrin, as it is more delicate in reaction; that is, it is a little more difficult to digest than the fibrin, thus showing retarding effects to a finer degree. However, when the latter substance is employed in the process, the work must not be delayed; in other words, after digestion has continued the desired number of hours, the undissolved fibrin should be quickly filtered, washed, and weighed; for fibrin decomposes rather quickly in the air, and by that means some of the undissolved substance might be lost, which, of course, would lead to erroneous results.

As an artificial gastric juice the following proportion was used: Two-tenths gram of purified pepsin dissolved in 10.2 cc. hydrochloric acid (sp. gr. 1.14), and this then made up to a liter.

[1] Care must be taken to add only just enough of the reagent to render the liquid very faintly acid. It must be remembered that albumin is very soluble in a slight excess of the acid.

Gastric juice prepared by simple extraction from pigs' stomachs with hydrochloric acid is not only not constant, but also often faulty in its action. These extracts contain slime-like albuminous bodies (not further understood) which contaminate the digestion. In order to avoid this, Kühne[1] recommends a juice prepared in the following manner:

"The prepared mucous membrane of the pig's stomach is digested six days at 40° C. with seven times its quantity of a five-tenths per cent. hydrochloric acid solution. Saturate now directly with ammonium sulphate; collect the precipitate as completely as possible, and wash with water. Dissolve in digestion hydrochloric acid (five-tenths per cent.) five times the amount of the membrane taken, which contains (0.25 per cent.) thyme oil, and again digest one day at 40° C. Saturate now with ammonium sulphate. The residue ('purified pepsin') is used for the digestion by suspending it in digestion hydrochloric acid."

To avoid the difficulty and loss of time attending the preparation of pepsin, the powdered article from the laboratories of Armour & Co. is recommended. If this extract is used, the juice should be made up in the above proportion: *viz.*, two-tenths gram pepsin, and 10.2 cc. hydrochloric acid (sp. gr. 1.14) dissolved in one liter of water.

For the intestinal digestion the artificial pancreatic juice was made by dissolving a mixture of three grams pancreatine (procured of Armour & Co.) and fifteen grams sodium bicarbonate in one liter of water. The pancreatic solution may, however, be prepared in the following manner:

After removing the fat from the pancreas of a beef, divide that organ finely (with a sausage mill or chopping knife). Triturate with fine, clean sand, and let stand twenty-four to thirty-six hours at 14°. Now treat the mixture with glycerol and water, employing for every 400 grams pancreas one liter of glycerol (sp. gr. 1.23) and one liter of water. After the lapse of three days press in a filter press, then through filter paper, and to the filtrate add five cc. chloroform (to prevent bacterial changes). Preserve in a cool place. When used, one gram sodium bicarbonate is added to each 100 cc. of the trypsin solution.

[1] *Zeit. f. Biol.*, **22**, 426–428.

In carrying on my experiments a control test, consisting of a mixture of 100 cc. of the digestive liquid and one gram of the substance to be digested (blood fibrin or egg-albumin), was placed in a 150 cc. flask, immersed in a water-bath, and subjected to a temperature of from 38° to 40° C., until complete digestion was manifest. Then, at the same time, and under the same conditions, similar mixtures, but with the addition of varying quantities of the body to be tested, were subjected to a like treatment. When the digestion of the control test was completed, all of the tests were cooled to the temperature of the laboratory, and then filtered and washed through tared filter papers. After drying, they were weighed, using the control filter paper as a control weight, and the amount of the undigested material thus calculated.

It can be seen from the method of procedure that my results are, to a certain extent, approximate. They are, however, accurate enough to show distinctively the behavior of the substances tested toward the digestive ferments.

I have grouped the substances with which I worked under the following heads, and this order will be adhered to in their discussion:

I. Digestion retarded even after prolonged treatment:

a. *Peptic:*
Picric acid.
Tropaeolin ooo.
Metanil yellow.

b. *Pancreatic:*
Bismark brown.
Cinnamon.
Formol.

II. Digestion ensues only after prolonged treatment:

Peptic:
Salicylic acid.
Oil of wintergreen.

III. Digestion progresses normally:

Peptic and Pancreatic:
Essence of peppermint.
Chrysoidine.
Safranine.
Methylene blue.

PICRIC ACID, $C_6H_2(NO_2)_2OH$.

The following results were obtained:

PEPTIC DIGESTION.

Test.	Amount of substance. Gram.	Amount of albumin. Gram.	Duration of experiment. Hours.	Material not digested. Gram.
1	0.00	1	6	0.00
2	0.60	1	6	1.00
3	0.30	1	6	0.92
4	0.20	1	6	0.76
5	0.10	1	6	0.55
6	0.06	1	6	0.32

PANCREATIC DIGESTION.

1	0.00	1	12	0.00
2	0.60	1	12	0.00
3	0.30	1	12	0.00
4	0.20	1	12	0.00
5	0.10	1	12	0.00
6	0.06	1	12	0.00

From the above results it will be seen that while the acid had a distinctively depressing effect on the peptic ferment—as is shown even in test No. 6, where the amount of the acid was only one part in 1,666 parts of the solution—yet its deportment toward the pancreatic ferment was perfectly normal.

The presence or absence of digested albumin in the solution may be proved by the addition of a solution of tannin, which reagent precipitates albuminous bodies.

TROPAEOLIN 000 No. 1, $NaSO_3.C_6H_4.N:N.C_{10}H_6OH$.

PEPTIC DIGESTION.

Test.	Amount of substance. Gram.	Amount of albumin Gram.	Duration of experiment. Hours.	Material not digested. Gram.
1	0.00	1	6	0.00
2	0.60	1	6	1.00
3	0.30	1	6	0.96
4	0.20	1	6	0.84
5	0.10	1	6	0.70
6	0.06	1	6	0.48

Thus it will be seen that this body has a very deleterious effect in the peptic ferment.

The color was found to have no retarding effect on the intestinal digestion, the albumin in all of the tests dissolving completely at the expiration of twelve hours.

METANIL YELLOW, $NaSO_3.C_6H_4.N:N.C_6H_4.NH.C_6H_5$.

PEPTIC DIGESTION.

Test.	Amount of substance.	Amount of albumin.	Duration of experiment.	Material not digested.
	Gram.	Gram.	Hours.	Grams.
1	0.00	1	6	0.00
2	0.60	1	6	1.00
3	0.30	1	6	0.93
4	0.20	1	6	0.52
5	0.10	1	6	0.41
6	0.06	1	6	0.32

This color, like the two preceding, has a markedly depressing effect on peptic ferment, but none at all on the pancreatic.

BISMARK BROWN, $C_6H_4(NH_2)—N—N—C_6H_3(NH_2)—NH_2.2HCl$.

PANCREATIC DIGESTION.

Test.	Amount of substance.	Amount of albumin.	Duration of experiment.	Material not digested.
	Gram.	Gram.	Hours.	Gram.
1	0.00	1	12	0.00
2	0.60	1	12	1.00
3	0.30	1	12	0.88
4	0.20	1	12	0.63
5	0.10	1	12	0.50
6	0.06	1	12	0.26

This color neither prevented nor delayed the peptic digestion.

The addition of Bismark brown to the pancreatic juice produced a heavy precipitate, consisting of the free color base. Therefore, control tests had to be made for these experiments. This was done by subjecting the same amount of the color to treatment similar to that of the test then being made—but without the addition of the substance to be digested—and after filtration, by using this precipitate and filter paper as a control weight.

In order to show that the depressing action on the ferment was caused by the Bismark brown itself, rather than by any mechanical influence which might have been produced by the presence of the precipitate in the solution, another test was made, wherein the precipitate was filtered off before the addition of the albumin, and the clear filtrate used as the digestion fluid. The result of this experiment was that the action of the ferment

was interfered with to the same extent as in the tests in which the precipitate was present.

CINNAMON.

The spirit of essence of cinnamon, prescribed by the U. S. Pharmacopoeia, is made up in the following proportions: Ten parts (one oz. av.) oil of cinnamon, and ninety parts alcohol.

The essence, prepared as given above, was used in the following experiments:

PANCREATIC DIGESTION.

Test.	Amount of substance.	Amount of albumin.	Duration of experiment.	Material not digested.
	Drops.	Gram.	Hours.	Gram.
1	00.0	1	12	0.00
2	30.0	1	12	1.00
3	20.0	1	12	0.90
4	10.0	1	12	0.68
5	5.0	1	12	0.24

No disturbance of the action of the peptic ferment by the introduction of this substance was produced, the digestion of the albumin in all of the experiments keeping pace with that of the control test.

FORMOL.[1]

A forty per cent. solution of formic aldehyde was used in these experiments.

PANCREATIC DIGESTION.

Test.	Amount of substance.	Amount of albumin.	Duration of experiment.	Material not digested.
	Drops.	Gram.	Hours.	Gram.
1	00.0	1	12	0.00
2	35.0	1	12	1.00
3	25.0	1	12	0.82
4	15.0	1	12	0.60
5	10.0	1	12	0.44
6	5.0	1	12	0.18

As in the case of the two preceding substances, formol had no apparent effect on peptic digestion.

It is seen from the above tests that this preservative has a very depressing action on the pancreatic ferment, even one part in 2,000 parts of the solution (test No. 6) being sufficient to distinctively retard digestion.

[1] Formula (?) $C(H)_2(OH)_2$. *Cf. Chem. Ztg., 1890*, 1408.

Salicylic Acid, $C_6H_4(OH).COOH$.

This body was found to retard the action of the peptic ferment, inasmuch as it considerably prolonged the time for complete digestion. Therefore, I made two series of tests: In the first, the amount of undissolved albumin at the completion of the digestion of the check test was recorded; in the second, the time necessary for complete digestion was noted. Thus:

Peptic Digestion.

Test.	Amount of substance.	Amount of albumin.	Duration of experiment.	Material not digested.
	Gram.	Gram.	Hours.	Gram.
1	0.00	1	6	0.00
2	0.60	1	6	0.85
3	0.30	1	6	0.56
4	0.20	1	6	0.34
5	0.10	1	6	0.25
6	0.06	1	6	0.10
1	0.00	1	6	0.00
2	0.20	1	11	0.00
3	0.10	1	9½	0.00
4	0.06	1	7	0.00

This acid is generally conceded to have a retarding action on digestion;[1] my reason for experimenting with it, however, was that I wished to compare the results with those of the following substance, wintergreen, the active principle of which is methyl salicylate.

Wintergreen.

For the following tests I used a preparation procured at a pharmacy, and recommended as the natural oil of wintergreen.

As in my experiments with salicylic acid, I conducted here two series of tests—first, the amount of material undissolved at the completion of the digestion of the control test was recorded, and second, the time for complete digestion was noted.

Peptic Digestion.

Test.	Amount of substance.	Amount of albumin.	Duration of experiment.	Material not digested.
	Drops.	Gram.	Hours.	Gram.
1	00.0	1	6	0.00
2	30.0	1	6	0.74
3	20.0	1	6	0.58
4	15.0	1	6	0.42
5	10.0	1	6	0.38
6	5.0	1	6	0.16

[1] Olaf Hammarsten: Physiological Chemistry, *1893*.

Test.	Amount of substance. Drops.	Amount of albumin. Gram.	Duration of experiment. Hours.	Material not digested. Gram.
1	00.0	1	6	0.00
2	15.0	1	12	0.00
3	10.0	1	11	0.00
4	5.0	1	8	0.00

By comparing the results of the experiments of salicylic acid and wintergreen a striking similarity of action on the peptic ferment will be noticed.

Wintergreen, as was expected from the behavior of salicylic acid, had no influence on the pancreatic digestion.

PEPPERMINT.

The essence, prepared according to the U. S. Pharmacopeia, *viz.*, oil of peppermint one fluid ounce, rectified spirits four fluid ounces, was used in my experiments with this body.

The action of peppermint on both the peptic and pancreatic ferments was found to be practically *nil.* For this reason it is useless to tabulate the different tests which were made. It is enough to say that the albumin in all cases, where the amount of the essence introduced varied from ten drops to three cc., digested in a perfectly normal manner; in other words, complete solution had taken place at the end of six hours for peptic and twelve hours for pancreatic.

The three coloring matters, chrysoidine, saffranine, and methylene blue, like the essence of peppermint, had no apparent effect on the action of either of the ferments. In all of the tests made, with the amount of the color introduced varying from 0.06 to 1.00 gram, the albumin was found to be completely dissolved at the end of the allotted time.

Summing up my experiments now, it will be seen that of the twelve substances with which I worked, three (picric acid, tropaeolin ooo, and metanil yellow) distinctly arrested peptic digestion, three (Bismark brown, cinnamon, and formol) pancreatic digestion, two (salicylic acid and wintergreen) partially arrested peptic digestion, and four (peppermint, chrysoidine, saffranine, and methylene blue) had no apparent effect on either of the ferments.

It is probably assuming too much for one to assert, or to state as having proved, that certain bodies completely arrest digestion. This will be seen at once if we consider that these artificial processes of digestion probably differ in a great many respects from those natural processes occurring in the stomach and intestines.

An answer to the question, "Does a substance seriously arrest digestion?" is perhaps not, strictly speaking, to be given in general, because the results obtained hold good only for the conditions under which the experiments were conducted; in other words, the neutralization capacity of the products of digestion must be taken into consideration. However, if we can show that some substances by themselves entirely, or nearly so, neutralize the action of the digestive ferments, we must naturally, and justly too, I think, infer that they have a very decided unwholesome effect on some of nature's functions. For, even if we assume that as fast as one portion of the digestive fluid is neutralized more is supplied until the right proportion for normal digestion is reached, one must see what a drain these inimical substances cause the organs to be subjected to. The organs supplying the fluids must be subjected to double, triple, or perhaps even more, work than that which normally they are required to perform; and the food too remains in the stomach and intestines a much longer period of time than usual, which fact alone would prove the arresting power of these foreign bodies.

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[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, UNIVERSITY OF MICHIGAN.]

A PRELIMINARY THERMOCHEMICAL STUDY OF IRON AND STEEL.

BY E. D. CAMPBELL AND FIRMAN THOMPSON.

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ALTHOUGH much work has been done upon the relation between the ultimate chemical composition and the mechanical and magnetic properties of iron and steel, very little has been done in the way of studying the question from a thermochemical standpoint.

In 1875 Troost and Hautefeuille[1] determined the amount of

[1] *Compt. rend.*, 80, 964.

heat evolved by treating several samples of pure iron, steel, and cast iron, with moist mercuric chloride, and came to the conclusion that the chemical compounds of iron and carbon were endothermic, that is, formed with absorption of heat, although those of manganese and carbon were exothermic. Later, in 1885, Osmond,[1] working in Troost's laboratory, obtained by dissolving samples of soft, medium, and hard steel, as well as white iron in ammonium copper chloride, results that contradicted those previously obtained by Troost and Hautefeuille. Osmond does not attempt to reduce the results obtained to calories, but states them in the number of degrees that 500 cc. of a saturated solution of ammonium copper chloride would be raised by dissolving one and a half grams of the metal operated upon.

He does not state the composition of the three steels and one white iron, except the per cents. of carbon, which were 0.17, 0.54, 1.17, and 4.10, respectively.

The rise in temperature for the three steels and cast iron is given by Osmond, as follows:

Metal.	Carbon.	Annealed.	Cold rolled.	Quenched.
1	0.17	2.151	2.247	....
2	0.54	2.111	2.207	2.222
3	1.17	1.895	2.018	2.056
4	4.10	1.419	....	1.632

From the fact that as the carbon increases the heat of solution of the annealed metals decreases, Osmond concludes that the combination of iron and carbon is accompanied by evolution of heat, not as Troost previously stated, with absorption of heat.

In order to bring out more clearly the influence of cold rolling and of hard metal, Osmond tabulates the above results, using the heat of solution of the annealed meal in each case as unity. The table given is as follows:

Metal.	Annealed.	Cold rolled.	Quenched.
1	1.000	1.045	....
2	1.000	1.045	1.052
3	1.000	1.065	1.084
4	1.000	....	1.150

Osmond says: "These results are conclusive; in every case, quenching, like cold rolling, is characterized by an augmentation in heat, which increases with the carbon content. We

[1] *Compt. rend.*, 100, 1228.

believe then, that the already very probable existence of two isomeric varieties of iron, α and β, may be considered as established.

"The crystallized, at least partially crystalline, α-iron is obtained by raising to full red heat, followed by slow cooling (annealing); it is transformed into β-iron (which the structure of quenched steel warrants us in regarding as amorphous) either by a permanent deformation at low temperature, or by rapid cooling from a red heat, but only then in the presence of carbon or of some other bodies (manganese, tungsten) exerting the same influence upon the properties of steel."

In order to maintain the allotropic hypothesis above stated, we must assume the heat of solution of α-iron to be less than that of β-iron, and yet although the difference in the heat of solution of the annealed and quenched specimens given increases with the increase in the per cent. of carbon, the absolute amount of heat evolved by the high carbon steel quenched, containing presumably all β-iron, is not so great as that of the low carbon annealed steel, presumably α-iron.

It was to try to determine whether carbon alone was responsible for the variations in the heat of solution of steels subjected to different heat treatments, that we undertook the work described hereafter.

The calorimeter employed consisted of four concentric beakers, the first and second, and third and fourth being separated by felt packing, leaving a closed air space between the second and third. The beaker in which the solution was performed was supported on a light cork ring cemented to the bottom of the inner beaker of the calorimeter, and was prevented from upsetting or touching the sides of this latter by thin strips of cork cemented to the sides of the inner beaker. The cover of the inner beaker consisted of a layer of felt held between disks of vulcanized rubber. This cover fitted close inside the inner beaker of the calorimeter and was perforated for the admission of the thermometers and stirrer.

The thermometers had a range of 10° each and were graduated to fiftieths of a degree. The stirrer, which extended almost to the bottom of the beaker in which the solution was performed, consisted of a glass rod bent at its lower end so as to stir the

entire solution and provided with small pieces of rubber cemented to it in such a way that they would sweep the entire bottom of the beaker, thus stirring up particles of metal and hastening the solution. Without the use of this device it was found impossible to get complete and certain solution in a short time, while with its use the time did not usually exceed fifteen to twenty minutes.

The stirrer was actuated constantly during the work by a water motor, the belt from which passed through a small hole in the wall of the constant temperature room in which the experiments were performed. The solution of all the samples was made in a slightly acid solution of potassium copper chloride made by dissolving the following constituents.

	Grams.
$CuCl_2$, $2H_2O$	368.24
KCl	325.80
HCl (41 per cent. HCl)	255.01
H_2O	1995.26

The constituents were accurately weighed out in each case on a large balance having a capacity of five kilos, and sensitive with this load to five milligrams, so that all solutions used throughout the work were practically identical.

The stock solution, after making, was allowed to stand over night, and was then filtered through asbestos and kept in a constant temperature room until ready for use. The mean specific heat of this solution was calculated from the weight of the constituents, using the following specific heats: Water 1, copper 0.095, potassium 0.164, chloride 0.1221, hydrogen in hydrochloric acid 3.41.

The mean specific heat of this stock solution, using these constants, was 0.748. The water equivalent of the beaker in which the solution was effected, of the immersed portion of the stirring rod, and the thermometer bulbs, was calculated from the weight of these, using 0.177 and 0.033 as specific heats of glass and mercury respectively. Although there may be a slight absolute error in the reduction of the temperatures observed to calories, owing to the specific heats used, since the same solution and apparatus were used throughout the work, the results were strictly comparable one with another, and the

absolute values are probably not more than one or two per cent. above or below those recorded.

The method of making the determinations was to put in the weighed beaker a weighed amount, usually about 275 grams of potassium copper chloride. The beaker was then placed in the calorimeter, with the cover on, and allowed to come to constant temperature. Since the stock solution was always kept in the constant temperature room the beaker containing the solution did not have to stand in the calorimeter more than about half an hour before the sample of steel could be added.

The sample of iron or steel was prepared by filing, or pounding the metal when too hard to file, but in all cases was reduced to a powder, fine enough to pass through a sieve with seventy meshes to the inch. This fine subdivision was necessary in order to insure rapid solution. When the temperature of the calorimeter had become constant two grams of the finely divided iron or steel were introduced into the beaker, the cover being temporarily raised for this purpose, and the stirrer was started. Solution was rapid, the maximum temperature in almost all cases being attained within fifteen to twenty minutes. The usual rise was from 5° to 7°. In one case, when the time of solution was unusually prolonged, about forty minutes being required, an allowance was made for loss by radiation. With temperature of the beaker 6° above that of the initial temperature, this loss was found to be 0.24° per hour. This correction had to be made only in one case.

The method of subjecting the different steels to heat treatment was as follows: Steel to be annealed was placed as far as possible out of access of air and heated to a temperature of between 900° and 1,000° and cooled very slowly. Quenched or hardened specimens were prepared from pieces of the annealed metal. Pieces of the steel usually weighing from 50 to 100 grams were placed in a porcelain tube having an internal diameter of about twenty mm. This tube was wrapped with two layers of asbestos paper and slipped inside an iron tube which extended about thirty cm. beyond the end of the porcelain tube.

The center of the iron tube, the portion containing the specimen to be heated, passed through a Hoskins gasoline furnace in such a way that the tube for a distance of from fifteen to eighteen

cm. could be easily raised to any desired temperature up to 1,200° C. Through the porcelain tube was introduced the thermal couple of a Le Chatelier pyrometer, the thermal junction being in direct contact with the piece of steel under treatment. The pyrometer had been carefully graduated and we think the temperatures given are accurate within probably 5° or less. The other end of the iron tube was kept closed during the heating by a cork in order to avoid oxidation. When everything was ready the temperature of the tube was slowly raised, the time usually being from twenty to forty minutes until the pyrometer indicated that the bar was at the desired temperature. When this was attained the cork was removed from the end of the tube and by quickly tilting the latter the piece of steel was dropped into ice-water at a temperature of from 4° to 5°. After the operation corrections for the temperature of the galvanometer, etc., was made, and the actual temperature at the moment of tilting the tube was calculated.

The heat of solution of the various samples of steel is shown in the following tables, Table I showing the influence of composition and varying heat treatment on the heat of solution, Table II showing heat of solution of other samples. The numbers given in the tables are the averages of at least two duplicates; the difference between two determinations on the same sample seldom exceeded four calories and only in one case was it six:

TABLE I.

Showing Influence of Chemical Composition and Heat Treatment on the Heat of Solution.

Experiment No.	Name of metal.	Chemical composition.					Heat treatment.		Calories evolved per gram of Fe + Mn.
		C.	Mn.	P.	S.	Si.		Quenched from $x°$.	
1	Pure iron wire	0.018	none	0.050	0.013	0.023	annealed	....	659.6
2	Car. H	0.09	0.22	0.016	0.023	....	"	....	629.1
3	" "	0.09	0.22	0.016	0.023	....		714°	637.0
4	" "	0.09	0.22	0.016	0.023	....		825°	650.9
5	" "	0.09	0.22	0.016	0.023	....		925°	684.7
6	" "	0.09	0.22	0.016	0.023	....		1025° Outside of bar.	712.3
7	" "	0.09	0.22	0.016	0.023	....		1025° Inside of bar.	705.9
8	Cl. 5	0.10	0.484	0.119	....	....	annealed	....	632.9
9	" 5	0.10	0.484	0.119	....	....		719°	651.2
10	" 5	0.10	0.484	0.119	....	....		825°	676.0
11	" 5	0.10	0.484	0.119	....	....		928°	707.6
12	" 5	0.10	0.484	0.119	....	....		1028°	741.1
13	N. S. 5	0.37	0.820	0.160	....	....	annealed	....	587.3
14	" 5	0.37	0.820	0.160	....	....		728°	626.3
15	" 5	0.37	0.820	0.160	....	....		827°	652.2
16	" 5	0.37	0.820	0.160	....	....		923°	675.1
17	" 5	0.37	0.820	0.160	....	....		1027°	760.6
18	Car. I	1.22	0.780	0.098	0.068	0.058	annealed	....	635.1
19	" "	1.22	0.780	0.098	0.068	0.058		719°	641.9
20	" "	1.22	0.780	0.098	0.068	0.058		750°	686.6
21	" "	1.22	0.780	0.098	0.068	0.058		825°	696.7
22	" "	1.22	0.780	0.098	0.068	0.058		923°	717.3
23	" "	1.22	0.780	0.098	0.068	0.058		1023°	755.6
24	T. S. D.	1.28	0.330	0.018	0.006	....	annealed	....	628.9
25	" " "	1.28	0.330	0.018	0.006	....		1025°	693.0

TABLE II.

Heats of Solution of Other Samples.

Experiment No.	Name of metal.	Chemical composition. C.	Mn.	P.	S.	Si.	Heat treatment.	Calories evolved per gram of Fe + Mn.
27	C. R. M. Co. 5	0.36	1.25	0.122	0.128	0.046	Normal.	560.7
28	Car. F.	0.55	0.70	0.027	0.026	....	Annealed.	562.0
29	" "	0.55	0.70	0.027	0.026	....	Hardened and reheated to 275°.	639.4
30	Cast steel	0.76	0.27	0.017	trace	0.234	Annealed.	583.1
31	No. 5. Char. pig iron	c 1.70 g 1.95	trace	0.260	....	0.262	Normal.	620.0
32	Pure carbide of iron	6.64	none	0.026	....	....	Annealed.	647.3
33	Swed. bar iron	....	....	....	....	....	Normal.	670.0
34	Special iron	3.22	0.33	0.018	0.006	....	Poured while molten into cold water.	756.0
35	" "	3.±	0.33	0.944	0.006	....	Poured while molten into cold water.	798.0
36	Pure Cu. wire	...	....	....	....	....	Normal.	60.2
37	" " "	...	....	....	....	....	Cooled slowly from 1,000°.	66.3
38	" " "	...	....	....	....	...	Quenched from 940°.	58.2

The following points seem to be indicated by the results in Tables I and II.

First. In annealed metal, owing to the heat of formation of compounds of iron with carbon, the heat of solution diminishes as the per cent. of carbon increases, until after the saturation point (eight-tenths to nine-tenths per cent.) is passed, when, owing probably to the endothermic formation of non-crystalline cementite, the heat of solution increases again, but never reaches that of pure iron. This is shown in experiments 1, 2, 30, 24, 31.

The heat of solution of the last mentioned may be somewhat lowered by the presence of phosphorus and silicon, the decomposition of whose compounds would almost certainly absorb some heat.

Second. The presence of manganese, when combined with carbon in annealed metal, diminishes very markedly the heat of solution, owing to the greater stability of the compounds of manganese and carbon, compared with that of the corresponding compounds of iron. If there is not sufficient carbon to combine with the manganese, or if the carbon is above the saturation point, the substitution of manganese for iron seems to increase the heat of solution slightly, owing to the higher heat of formation of manganous chloride compared with that of ferrous chloride. This influence of manganese on heat of solution of annealed metal is clearly shown in experiments Nos. 2 and 8, 13 and 27; 28, 24, and 18.

Third. In the quenched metal, manganese seems to behave exactly the reverse from that in the annealed steel, the effect being to very notably increase the heat of solution, the increase being more marked the higher the temperature from which the steel is quenched. This is shown on comparing the heats of solutions of experiments Nos. 7 and 12, 17, 23 and 25.

Fourth. That phosphorus plays a considerable part in determining the heat of solution is shown by experiments 34 and 35, although these cannot be easily compared with the above, since the temperature from which the metal was quenched is not known, but must have been not far from 1,100° or 1,200°, as the metal was perfectly fluid when poured into cold water.

Fifth. The results obtained on copper (experiments 36, 37,

and 38) confirm those of Osmond, that is, that heat treatment has but slight influence on the heat of solution.

The next series of experiments undertaken was to determine the influence of reheating or "tempering" hardened steel upon its heat of solution. The steel selected for this purpose was the steel marked T. S. D. (see experiment 24, Table I). The steel had been hardened by heating to between 900° and 1,000° and quenching in ice-water. On account of the low phosphorus present in the metal we knew that it would be useless to attempt to get such steel as this in a sufficiently fine state of division for the work, if the metal was tempered before subdividing. High-grade tool steel of this class, if hardened and tempered, would be too hard to file and too tough to pulverize in a steel mortar, so that we resorted to the plan of pulverizing a considerable amount of the hardened metal and reheated the powdered steel in a stream of hydrogen or of nitrogen in order to avoid oxidation. For reheating to temperatures up to and including 400° from five to six grams of the bright powdered steel was placed in a large test-tube provided with a three-hole stopper; through one hole there was a tube for the purpose of conducting pure dry hydrogen nearly to the bottom of the test-tube; through the second hole a nitrogen filled thermometer was introduced, the bulb of the thermometer reaching to the bottom of the test-tube and being surrounded by the steel; the third hole was provided with a piece of tubing drawn down to a fine point, serving as an escape for the hydrogen.

For heating to 100° C. the test-tube so arranged was kept in a water-bath for twenty-four hours, the air in the test-tube having been displaced by pure dry hydrogen. For raising the temperature to from 200° to 400°, inclusive, the following device was employed: A piece of pig iron weighing about five kilos was drilled nearly through, the hole being somewhat larger than the diameter of the test-tube used. A little sand was placed in the hole, then the test-tube inserted deep enough so that the steel was a little below the center of the bar; the space around the test-tube was then filled with sand. This arrangement secured the slow, even heating of the sample. When the air in the test-tube had been completely displaced by dry hydrogen, the bar was slowly heated until the thermometer indicated the desired

temperature. The light was then turned out and the tube allowed to cool in hydrogen. For temperatures higher than 400° the powdered steel was placed in a porcelain combustion boat contained in a porcelain combustion tube. One end of this latter was closed by a one-hole stopper through which the dry hydrogen or nitrogen employed was conducted. In the other end of the combustion tube the thermal couple of the pyrometer was introduced in such a way that the thermal junction rested on the boat containing the steel. The portion of the tube containing the boat was then slowly heated in an ordinary combustion furnace, or for higher temperatures in a gasoline furnace, until the desired temperature was attained, then allowed to cool, the current of hydrogen or nitrogen being kept up during the cooling. Bright powdered steel underwent no apparent change in color, only when heated to 1,024° the mass showed a slight tendency to stick together.

In addition to determining the heat of solution of these reheated samples, we made colorimetric carbon determinations, using the annealed steel carbon, 1.28 per cent., as a standard.

The results of the reheating on the heat of solution and the color carbon determinations are embodied in Table III.

TABLE III.

SHOWING INFLUENCE OF TEMPERING ON HEAT OF SOLUTION AND COLOR CARBON TEST.

Experiment No.	Temperature to which metal was raised.	Gas used.	Calories evolved per gram Fe + Mn.	Carbon indicated by color.
39	0		688.0	1.14
40	100°	Hydrogen	685.8	1.14
41	200°	"	685.8	1.14
42	250°	"	673.9	1.14
43	300°	"	666.0	1.18
44	400°	"	662.5	1.20
45	500°	"	657.6	1.27
46	609°	"	634.7	1.27
47	715°	"	631.8	1.16
48	759°	"	687.4	1.03
49	1024°	"	705.6	0.29
50	1024°	Nitrogen	583.3	0.57
51	1024°	"	560.6	0.73

It will be noticed in this table that the heat of solution decreases and the apparent per cent. of carbon increases with

the temperature to which the metal is reheated until the critical point Ac_1 is passed. When the critical point Ac_1 is passed the hydrogen seems to combine with the carbon and the heat of solution rises very markedly. When the gas used was nitrogen, the temperature being over 1,000°, the nitrogen removes the carbon, part at least forming cyanogen, as was shown by passing the nitrogen through potassium hydroxide and precipitating silver cyanide with silver nitrate, after acidification with nitric acid. The heat of solution of the metal heated and cooled in nitrogen is very much lowered, being in fact what we might expect of ordinary annealed metal of the indicated per cent. of carbon, as brought out in Table I.

Why iron heated to high heats in hydrogen and cooled in this gas should increase the heat of solution, we are not at present prepared to state, but we hope to investigate this point in the near future.

The last set of experiments was made to show the influence of cold working upon the heat of solution and tensile strength of pure iron. The sample used was one of very fine No. 36 pure, bright iron wire twenty-two hundredths mm. in diameter and of the composition shown in experiment No. 1. In subjecting this to heat treatment small coils of the wire were placed in a porcelain combustion tube and slowly raised to the temperature indicated, as shown by the Le Chatelier pyrometer, a current of dry hydrogen being kept up during the operation.

As in the work on reheating powdered steel the metal was cooled in a current of hydrogen, after being heated to the desired temperature. After the heat treatment a portion of the metal was used for making tensile strength determinations and part was dissolved for determining the heat of solution. The results of this work are given in Table IV.

TABLE IV.

SHOWING EFFECT OF REHEATING ON HEAT OF SOLUTION AND TENSILE STRENGTH OF COLD DRAWN IRON WIRE.

Experiment. No.	Temperature to which wire was raised.	Calories evolved per gram of Fe + Mn.	Tensile strength. Kilos per square mm.	Tensile strength. Pounds per square inch.
52	0	802.1	96.8	135,520
53	400°	750.6	74.2	103,880
54	609°	663.9	42.1	58,940
55	765°	659.6	....	....

The following interesting relation is brought out in the above table. The diminution in tensile strength is almost exactly proportional to the diminution in the heat of solution. Thus, in reheating to 600° the heat of solution has fallen from 802.1 to 663.9, or 138.2 calories, while the tensile strength has fallen from 96.8 to 42.1, or 54.7 kilos per square mm., or the tensile strength has been reduced at the rate of 0.395 kilos per square mm. for each calorie diminution in the heat of solution. That this holds very nearly, is shown by the results obtained by reheating to 400°. The heat of solution has diminished 51.5 calories, which, if the tensile strength diminishes proportional to the falling off in the heat of solution, would indicate a tensile strength of 76.46 kilos, whereas the actual results gave 74.2 kilos.

If the increase in tensile strength accompanied by increase in heat of solution of this wire is due to allotropy in the iron induced by cold working, then the hardening of steel cannot easily be attributed to the same allotropic change, since the drawn iron wire has a higher heat of solution and hence presumably a higher proportion of non-α-iron than any of the hardened steels, and yet the wire is comparatively very soft, while many of the steels are hard enough to scratch glass easily.

Although a number of interesting facts have been brought out in the above work, the data obtained are yet too few to enable reliable conclusions to be drawn in regard to phenomena complicated by so many factors as are present in the work under examination.

We hope to continue the work along the lines indicated in the present paper and to obtain results more satisfactory than those herein described.

ANN ARBOR, MICH., June 24, 1897.

NOTE.

The Fifteenth Annual Report of the Committee on Indexing Chemical Literature, just received from the chairman, Dr. Bolton, shows very great progress. Dr. Bolton's pioneer work has borne good fruit. Most books on chemistry now issued make some attempt at a bibliographic account of the subject-matter greatly to the benefit and convenience of the reader. Copies of the report may be obtained of the chairman, Dr. H. Carrington Bolton, Cosmos Club, Washington, D. C.

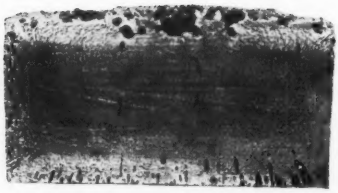

Fig. 8.

OBITUARY.

PROF. EDGAR MCCLURE, professor of chemistry in the University of Oregon, Eugene, Ore., met his death on the ice slopes of Mt. Rainier, in the State of Washington, on the 27th day of July last. He was engaged at the time in the descent of the mountain, after having successfully made the ascent, and taken all the necessary measurements to determine the height of the mountain. When near the foot of the snowfield, night came on, and in the uncertain light his footing gave way, and he lost his life upon the rocks below.

NEW BOOKS.

THE PHASE RULE. BY W. D. BANCROFT. Large octavo. viii + 255. Ithaca, N. Y.: The Journal of Physical Chemistry. 1897. Price $3.00.

In this book an attempt is made "to present the subject of qualitative equilibrium from the point of view of the Phase Rule and of the Theorem of Le Chatelier, without the use of mathematics." Such facts as bear upon the states and changes of equilibrium of a system of bodies, as determined by the temperature, pressure, and concentrations of its components, are here brought together and discussed in a methodical manner. Generally speaking, this has been admirably done, and the book should be of interest to chemists of every persuasion.

In an introductory chapter, the author defines and illustrates "phase" and "component," and states and explains Gibbs' Phase Rule and Le Chatelier's Theorem. He then passes to the consideration of a system consisting of one component; here the treatment of such familiar notions as boiling-point, sublimation, etc., will prove a revelation to many. Most of the book is devoted to systems containing two and three components, as the greater part of the experimental work on this subject has been confined to such systems. The concluding chapter gives the general theory of systems made up of four components, together with a *critique* of the meager experimental data pertaining to them.

The book has an especial value in that the author points out here and there in his theoretical discussions where further experimental work ought to be done, and, as has often been said,

the proposing of a good subject for research is often as difficult and as valuable as its experimental prosecution.

Also worthy of mention and commendation is the sharpness of definition of certain terms too commonly used in rather a loose sense. To be fair, however, it must be added that the author does not always show a just and impartial appreciation of experimental facts; if he can't give data a clear explanation in the light of his theory, then, he too often concludes, the data themselves must be in error. This is done, in one case, at least, where the author has not fully grasped the experimental facts.

The book, in places, is rather tedious reading, principally for this reason · The author often enters into the minutest details right in connection with general discussions and conclusions, which is somewhat bewildering and confusing. This might have been avoided, perhaps, by a more liberal use of foot-notes. There are also certain notions original with the author and occupying rather a prominent position throughout the work that do not seem to require so much emphasis, especially as they have not been adopted generally; thus the distinction between solvent and "solute," between "fusion" and "solubility" curves is hardly scientific or necessary.

Although the suppression of mathematics in the book may make it more acceptable to those chemists who are lacking in mathematical training, yet a certain amount of mathematical treatment of some points would have rendered them more intelligible as well as more in keeping with the historical development of the subject. C. E. LINEBARGER.

BOOKS RECEIVED.

An Electrolytic Method of Determining the Temperature of Soils. By Milton Whitney and Lyman J. Briggs. Bulletin No. 7, Division of Soils, U. S. Department of Agriculture, Washington, D. C. 15 pp.

An Electrolytic Method of Determining the Soluble Salt Content of Soils, with Some Results of Investigations on the Effect of Water and Soluble Salts on the Electrical Resistance of Soils. By Milton Whitney and Thos. H. Means. Bulletin No. 8. Division of Soils, U. S. Department of Agriculture, Washington, D. C. 30 pp.

Bulletin of the United States Geological Survey, No. 148. By F. W. Clarke and W. F. Hillebrand. U. S. Geological Survey, Washington, D. C. 306 pp. A Discussion of Methods of Analysis; Analyses of Various Rocks, Igneous and Crystalline, Stony Meteorites, Meteoric Iron, Sandstones and Cherts, Carbonate Rocks, Slates and Shales, Clays, Soils, etc., arranged and tabulated by F. W. Clarke.

Fertilizer Analyses of the Fertilizer Control. Special Bulletin No. 47. The North Carolina Agricultural Experiment Station, Raleigh, N. C., June 26, 1897. 8 pp.

Field Experiments with Sugar Cane. Seasons of 1893, 1894, and 1895. By Hubert Edson. Bulletin No. 12. Calumet Plantation, Patterson, La. 59 pp.

Ninth Biennial Report of the Director of the North Carolina Experiment Station, for the Two Years ending January, 1897. H. B. Battle, Director, Raleigh, N. C. 157 pp.

Sixth Annual Report of the Bureau of Labor, Statistics, and Mines, to the Governor and Fiftieth General Assembly of the State of Tennessee. 1896. A. H. Wood, Commissioner of Labor and Inspector of Mines, Nashville, Tennessee. 318 pp.

Geological Survey of Canada. G. W. Dawson, Director. Annual Report (New Series) with numerous maps. Vol. viii. 1895. Ottawa, Canada. xii + 154A + 120D + 184J + 387L + 59R + 103S pp. Price (with maps) $1.00.

The Cost of Plant Food in Connecticut, Spring Months of 1897. Bulletin No. 124. Connecticut Agricultural Experiment Station, New Haven, Conn. June, 1897. 11 pp.

The Elements of Electro-Chemistry Treated Experimentally. By Dr. Robert Lüpke. Translated from the second revised and enlarged edition by M. M. Pattison Muir. London: H. Grevel & Co. Philadelphia: J. B. Lippincott Co. 1897. xv + 223 pp. 54 figures in the text. Price $2.50.

The Composition of Prepared Cereal Foods. By E. E. Slosson. Bulletin No. 33. June, 1897. 14 pp. Wyoming Experiment Station, Laramie, Wyoming.

Incompatibilities in Prescriptions. For Students in Pharmacy and Medicine and Practicing Pharmacists and Physicians. By Edsel A. Ruddiman, Ph.D., M.D. 8vo., cloth. v + 264 pp. 1897. New York: John Wiley & Sons. Price $2.00.

Ninth Annual Report of the Texas Agricultural Experiment Station for the Calendar Year 1896. Agricultural and Mechanical College of Texas, College Station, Brazos Co., Texas. 12 pp.

Steer Feeding. Bulletin No. 41. Texas Agricultural Experiment Station, College Station, Brazos Co., Texas. 34 pp.

Elements of Chemistry. By Rufus P. Williams. viii + 412 pp. Boston: Ginn & Co. 1897. Price $1.20.

Water and Public Health. The Relative Purity of Waters from Different Sources. By James H. Fuertes. x + 75 pp. 1897. New York: John Wiley & Sons. Price $1.50.

Exercises in Practical Physiology. By Augustus D. Waller. Part III. Physiology of the Nervous System. Electro-Physiology. 91 pp. 1897. New York: Longmans, Green & Co. Price 90 cents.